Characterisation of Aerosols Using Carbon and Lead Stable Isotopes and Trace Elements.

Thesis

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Characterisation of Aerosols Using Carbon and Lead Stable Isotopes and Trace Elements.

By

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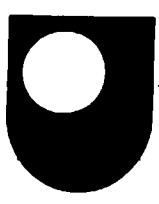

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This thesis is dedicated to the memory of my Grandfathers, Carmelo Carabott and Taddeo Cutajar who both supported me throughout my studies and whose loss is greatly felt.

Also in remembrance of Rachel Murphy and David Messenger who were supportive and generous to so many.

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I think this is a suitable point to add my thanks to S.O.U.P. and all its members, especially Andy, for helping me to regularly escape down a deep, dark, wet, cave and haul and 'shove' me out again. I would also like to recognise the importance that Rob and Mark played in reminding me that no matter how bad it all got, it could always get, just that little bit more..... sordid- thanks boys!

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Abstract

Ambient air contains a multitude of solid particles in a wide grain size range, commonly reffered to as atmospheric aerosol. Aerosols can be inserted into the atmosphere by a large number of processes, including water bubble bursting and wind injection, and can be derived from a numerous sources, including incinerators, smelters, vehicles, sea and soil/crust. Trace element characteristics have been used extensively to identify anthropogenic components within the atmosphere. However, methods such as, enrichment factors and pricipal component analysis can crudley discriminate between various sources of an element such as Pb. C and Pb isotopes have been found to have potential for the identification and characterisation of aerosol sources. Thus, when trace element characteristics and C and Pb stable isotopes are used in conjunction the sources of elements maybe characterised.

Aerosol samples were collected from two locations in the United Kingdom. The first at Milton Keynes consisted of a one year monitoring programme; the second in the South Wales region covered a broader geographic area in the hope of identifying discreet source areas. The aerosols were analysed for their Pb isotopic compositions, $\delta^{13}C$ values and trace element abundance.

At Milton Keynes, $\delta^{13}C$ values, Pb isotopic compositions and trace element abundance were found to vary considerable depending on wind direction, indicating multiple sources. At least three sources have been identified; vehicles, soils and point sources, such as incinerators. Aerosol Pb and trace element abundance were found to be influenced by rainfall, with rain having an apparent scavenging effect on Pb in the atmosphere. Temporal flucuations, both daily to montly, have been associated with these weather conditions.

Within the S Wales region two preliminary source zones of C and Pb were identified, with a possible third mixing zone; marine, industrial and rural/marine. Upon further investigation

these sources were suffieciently honed to characterise three source areas with two mixing zones;

(1) Rural

(2) Industrial

(3) Marine

(4) Industrial/Marine mix

(5) Vehicle/Marine mix

These zones were found to be wind direction dependent and did not alter annually.

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Chapter 1

Natural and anthropogenic sources of lead, carbon and trace elements

1.0 Introduction

Air pollution, such as smoke from heating and cooking fires and domestic waste odours, is by no means a new phenomenon. In fact it can be argued that air pollution has been characteristic of human living since the time when man first started to live in communities. However, it was the industrial revolution that heralded a rapid increase in anthropogenic[1] environmental pollution. Today, large quantities of anthropogenic substances are emitted into the atmosphere by industrial activities, most noticeably in the northern hemisphere (Völkening *et al.*, 1988). Power generation, heavy industrial processes and vehicle exhaust are the major anthropogenic contributors of pollutants such as sulphur dioxide (SO_2), oxides of nitrogen (NO and NO_2), carbon monoxide (CO), ozone (O_3), ammonia (NH_3), hydrocarbons, trace elements, such as lead (Pb), mercury (Hg), cadmium (Cd) and dust particles. These pollutants have wide-ranging effects, from the local reduction of visibility, detrimental health effects such as aggravating asthma and other respiratory diseases to global consequences such as the greenhouse effect. Of the major pollutants two of the most widely studied elements are carbon (C) and Pb. This is due to adverse biological and ecological effects (Arey *et al.*, 1988) of these elements; some C compounds are carcinogenic (Arey *et al.*, 1988; Lewats *et al.*, 1987) and Pb has been found to have adverse neurological effects (Engel *et al.*, 1971; Fachetti *et al.*, 1982, Zielhuis, 1991) on children.

[1] *Anthropogenic is defined as pollution produced by humankind.*

In fact, some of the most effective anti-pollution legislation in Britain was implemented through the study of C particulates within smog episodes. On the 5-11th December 1952, in London under stagnant weather conditions, the build-up and synergenic association of smoke coupled with SO_2 (smog) was found to have been responsible for an extra 3500 to 4000 deaths. This massive pollution episode was followed by the 1956 Clean Air Act which limited smoke and SO_2 emissions and dramatically reduced smog in Britain.

The other major pollutant which has had near world-wide legislation is Pb. This is because Pb has one of the highest emission rates of any metal. Lead anthropogenic emissions were estimated at 123,000 t/yr compared to 80,000 t/yr for Zn and 15,500 t/yr for Cu in 1979 (Nriagu and Davidson, 1986). These high emissions are due to Pb's application as an anti-knock agent in gasoline and its emission by industrial combustion processes (Pacyma, 1984; Nriagu, 1979a & b). The occurrence of Pb in atmospheric particles is of great interest due to adverse biological and ecological effects. Furthermore, although the commercial use of Pb is declining in developed countries it is still in common use and has therefore been widely studied. Lead also has considerable potential as a tracer of pollutant aerosol origin. It is of considerable value to be able to identify the source and examine the transport mechanisms of atmospheric Pb. This project has attempted to use C and Pb stable isotopes with trace element modelling to identify the sources of C and Pb within the Milton Keynes and S. Wales area.

The concentrations of major pollutant substances such as C and Pb have been monitored regularly since the 1950s in the U.S. and some European countries. The concentrations have risen for most of the monitored substances. The increased concentrations, medical evidence on the adverse health effects of Pb (neurological effects on children) and subsequent public concern, has caused governments to act and legislate to try and reduce the emissions of substances such as Pb. For instance, the European Union under directive 85/210/EEC required the maximum Pb content of petrol to be reduced to 0.15g/l (European Economic Community, 1985).

However, for legislation to be effective the sources of polluting elements must be known. It would be more helpful to legislators if the source of high concentrations of Pb or C could be identified. For example, possible sources in the vicinity of Milton Keynes include:

1. Natural sources :

(a) Soil and marine dust.

(b) Volcanic activity: Pb particulates are carried in the stratosphere and/or troposphere and then deposited many 100s' to 1,000s' km away.

2. Anthropogenic sources :

(a) local point sources such as vehicle emissions from the M1 motorway (a linear source).

(b) regional sources such as power stations and Pb smelters and incinerators.

It is questions like these that concentration data alone can not answer. The identification of Pb sources within the atmosphere is difficult to achieve because discriminating between Pb sources solely by Pb concentration is not possible. Two approaches have been devised:

1. The identification of the multi-elemental compositions of atmospheric particulates (Sweitlicki, 1989).

2. The use of Pb isotopic compositions of particulate Pb (Duce *et al*, 1980, Patterson and Settle, 1981, Rosman *et al* in 1993).

This project combines these two techniques in the hope of producing a comprehensive study. The use of C and Pb isotopes in conjunction with trace elements may hold the key to identifying sources of pollution within the atmosphere. This would be an invaluable tool for legislators to direct controls on the exact source of pollution and indeed to police existing legislation.

1.1 Lead isotopes in the environment

There are four stable isotopes of Pb: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. These isotopes are present in nature in the average proportions of 1:17:15:37 (Faure, 1986). Lead has a wide variation in isotopic composition between Pb ores of different geological formations (Table 1.0). The ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes are formed from the radioactive decay of U and Th, while ^{204}Pb has no radioactive progenitor: ^{238}Uranium decays to ^{206}Pb, ^{235}U to ^{207}Pb and ^{232}Th to ^{208}Pb. The isotopic composition of Pb ore therefore depends upon the original Pb, U and Th concentration and the age of the deposit. The isotopic composition is unaffected by normal chemical and physical processes, thus any Pb dispersed into the environment by smelters, petrol, coal combustion and other processes retains the characteristic Pb isotopic ratio of the original Pb ore from which it was derived. The Pb isotopic compositions for the ores listed in Figure 1 lie on a single curve, the Pb evolution curve (Figure 1.0).

The relative position of each Pb ore is determined by the history of the ore genesis. Thus, the older Pb ores are located to the lower left corner of the curve and the younger ones are located at the upper right part of the curve. This is because the Pre-Cambrian host rocks have the least radiogenic components, *e.g.* Broken Hill and Mount Isa in Australia and Bunker Hill, Idaho, USA. Any Pb ore with isotopic compositions more radiogenic than that of Quaternary Pb is known as anomalous Pb since these Pbs indicate a isotopically negative model age, for example, Tertiary Pb of Colorado, USA. This one formation can be explained by the Colorado Plateau being rich in U mineral deposits that decay into radiogenic Pb and thus 'shift' the Pb isotopic composition beyond the Quaternary region (Chow, 1970). Thus, the model ages lie in the future because they contain more radiogenic Pb than is compatible with a single-stage model (Faure, 1986). Chow and Earl (1972) analysed Pb isotopic ratios of coal and gasoline (Figure 1.1) The ratios indicated that Pb in coal is more radiogenic than Pb in the continental crust (gasoline Pb additive) and that

emissions of coal and gasoline could be distinguished. This discovery led to other environmental investigations.

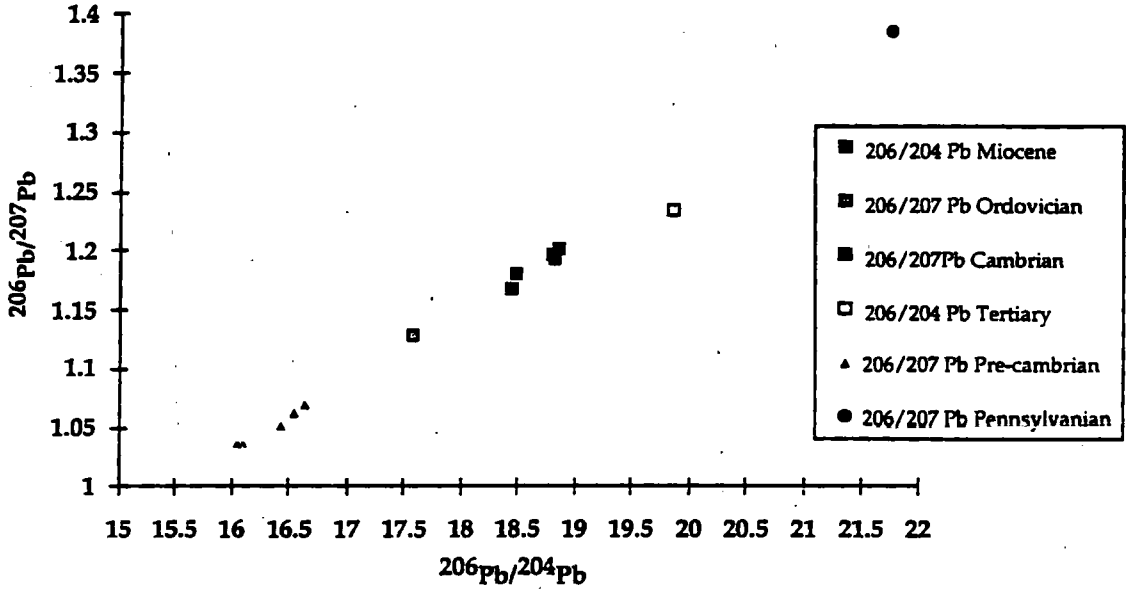

Figure 1.0
All Pb ore isotopic ratios lie on the Pb evolution curve (Chow, 1970).

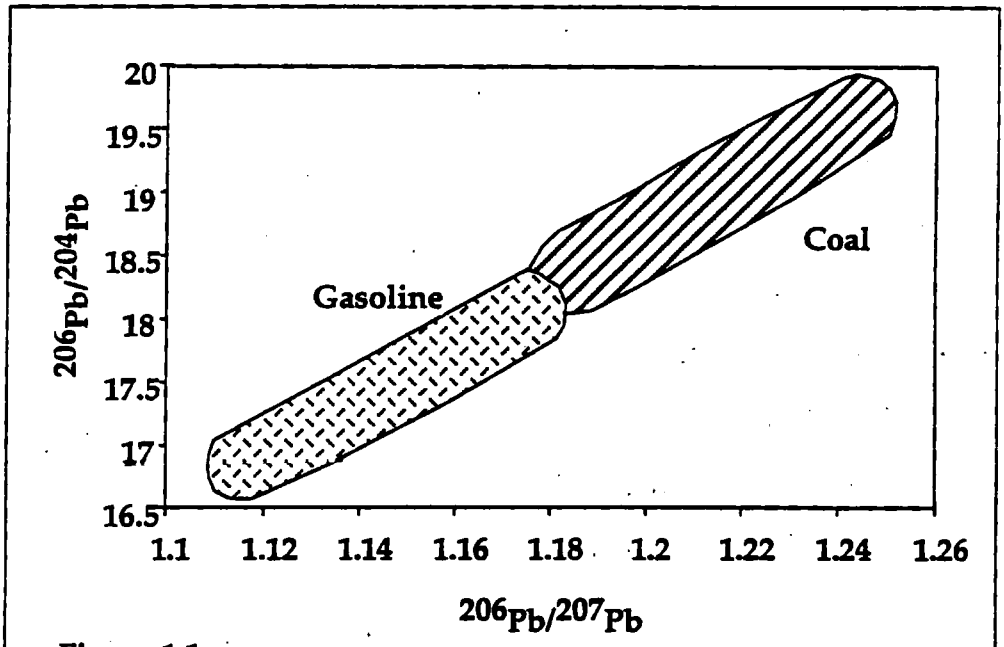

Figure 1.1
A comparison of Pb isotope ratios of coal and gasoline, indicating that gasoline and coal can be distinguished by Pb isotopic ratios (Chow and Earl, 1972).

Table 1.0

The isotopic compositions of Pb in a variety of Pb ores (Chow, 1970).

Country	District	Host rock age	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$	$^{208}Pb/^{207}Pb$
Missouri, USA	Mississippi valley	Pennsylv-anian	21.78	1.385	0.5342	2.555
Idaho, USA	Bunker Hill	Pre-cambrian	16.45	1.052	0.4525	2.250
Idaho, USA	Sunshine	Pre-cambrian	16.55	1.062	0.4497	2.362
Utah, USA	Tintic	Tertiary	18.50	1.179	0.4744	2.485
Colorado, USA	San Miguel	Tertiary	19.88	1.233	0.4979	2.476
N.W. Territory, Canada	Pine Point	Ordovician	18.47	1.166	0.4792	2.433
British Columbia, Canada	Bluebell	Cambrian	17.60	1.127	0.4738	2.379
British Columbia, Canada	Sullivan	Pre-cambrian	16.66	1.069	0.4578	2.335
Peru	San Cristobal	Miocene	18.87	1.201	0.4824	2.489
Australia	Mount Isa	Pre-cambrian	16.10	1.037	0.4464	2.323
Australia	Broken Hill	Pre-cambrian	16.07	1.037	0.4465	2.322
Mexico	Texo	Tertiary	18.84	1.191	0.4836	2.463
Yugoslavia	Trepca	Tertiary	18.83	1.195	0.4796	2.492

1.2 Lead in the environment

The element Pb is one of the oldest metals known to man. It was used in ancient Egypt for glazing pottery (7,000 to 5,000 B.C); the Hanging Gardens of Babylon were floored with sheet Pb to retain moisture and the Romans used Pb extensively for water pipes and plumbing - hence the chemical symbol Pb, taken from the Latin name, *plumbum*, for lead (Greenwood and Earnshaw, 1984). In fact the Romans extracted 6 to 8 million tonnes in four centuries. However, it was not until the industrial revolution that Pb in the environment increased greatly in concentration (Figure 1.2).

Today, Pb is used as an inert material in cast, rolled or extruded form, a greater tonnage is consumed as alloys. The major application for Pb is in storage batteries in which Pb-Sb (91: 9) alloy forms the supporting grid for the oxidising agent PbO_2 and the reducing agents (Kirk-Othmer, 1981 and Kuhn, 1977). Over 80% of this Pb is recovered and recycled.

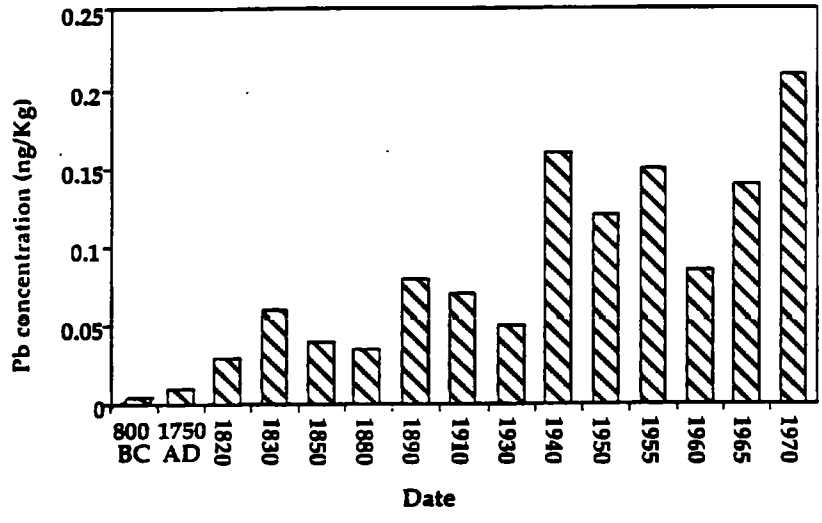

Figure 1.2
The concentration of ambient Pb in the environment has been observed to have increase dramatically from the beginning of the industrial revolution (Patterson and Chow, 1970).

Also, tin is used in conjunction with Pb in solders, fusible alloys and heavy duty bearing metals (Pb 5%). The latter have the characteristics of a hard compound embedded in a soft matrix and are used mainly in railway wagons and diesel locomotives.

Lead compounds are also used in pigments. Lead pigments are widely used from road markings to ceramic glazes and are used as rust-inhibiting primary paints for Fe and steel. Red lead (Pb_3O_4) is the traditional primer but Ca_2PbO_4 is also used. Lead chromate ($PbCrO_4$) is a yellow pigment used for road markings and an ingredient in many green paints and coloured plastics (Greenwood and Earnshaw, 1984). The element Pb also has mechanical applications such as ballast and bullet shot pellets.

World production of Pb in 1977 approached 3.5 million tonnes; the four main producers were USA (16%), USSR (15%), Australia (13%) and Canada (9%). The pattern of use of Pb compounds in a country is dependent upon whether organolead compounds are permitted as anti-knock additives in petrol for cars. Environmental legislation in both the USA and Europe is gradually eliminating the use of tetramethyl ($Pb(CH_3)_4$) and tetraethyl Pb ($Pb(C_2H_5)_4$). But at present, the largest contributors of Pb in the environment are organolead compounds burned as anti-knock additives.

1.3 Anthropogenic sources of Pb

There are 5 main anthropogenic sources of Pb in the atmosphere;

1. Vehicle exhaust emissions.
2. Coal and oil combustion.
3. Smelters.
4. Mine tailings/landfills.
5. Incinerators.

Of these 5 sources, the overwhelming contributors to atmospheric pollution are vehicle exhaust emissions. Mine tailings/landfills and incinerators are discussed in the trace element section, 1.4.

1.3.1 Vehicle exhaust emissions

The U.K. has over 23 million road vehicles which are a major source of air pollutants: Nitrous oxides (NO_X), hydrocarbons, carbon monoxide (CO), Pb, particulate matter and carbon dioxide (CO_2). The relative contributions within the UK of road transport for 1993 are stated in Table 1.1 . Between 1983 and 1994 the total distance travelled by road in the UK has increased by 35% to 689 billion passenger km. This equates to an increase from 288.1 to 421.9 billion vehicle km, an increase of 46% over the same period. This increase in vehicle km is almost entirely due to a 50% increase in the use of the car. Forecast traffic growths to 2025 provided by the Department of Transport (1995) show a potential increase

in cars and taxis of between 60% and 93% and for all traffic 61% to 98%. Road freight is also predicted to increase by between 81% and 168%.

Table 1.1

The contribution from road vehicles to total emissions of vehicle associated pollutants Department of Transport, 1995).

Pollutant	% Contribution from road vehicles. (1990)
VOC	45
NO_X	51
CO	91
Pb Particulates	90
Black smoke	52

Analysis of emissions for road transport from 1983 show that for all but black smoke, a peak emission was reached during 1989 to 1991 with the most recent estimates showing a downward trend (Department of the Environment, 1995). However, if predicted traffic growth continues this downward trend will be nullified by the next decade (SEIPH, 1995).

Some 180,998 tons of Pb (98.2%) is estimated to have originated from gasoline combustion in 1968 (Chow and Earl, 1972). In the UK the Department of Transport (1995) estimated that in 1993 some 1.5 thousand tonnes of Pb was emitted by road transport.

Lead is added to petrol as the organic liquids lead tetramethyl and tetraethyl, which when combusted are emitted as oxides, sulphides, halides and carbonates (Chamberlain, *et al.*, 1979). Vehicle exhaust consists primarily of Pb halides. The urban atmosphere however, has some Pb halides (PbBrCl) present but the main proportion of Pb in vehicle exhaust appears to be in sulphate forms ($(NH_4)_2SO_4.PbSO_4$ and $PbSO_4$).

1.3.11 The ambient chemistry of inorganic lead vehicle exhaust emissions

Table 1.2 shows that inorganic Pb compounds have been identified in an area without major industrial sources of Pb and indicates the problems associated with contamination close to

roads. This table and other studies (Hirschler *et al.*, 1957, Habibi, 1973, Biggins and Harrison, 1979 and O'Connor and Jaklevic, 1981) have established that PbBrCl is the major Pb compound emitted by vehicles, with α–2PbBrCl.NH_4Cl, β-2PbBrCl.NH_4Cl and PbBrCl.NH_4Cl in lower concentrations, emitted during driving in urban areas.

The other Pb compounds observed arise from the atmospheric chemical transformations of primary Pb compounds (Biggins and Harrison, 1979).

Indeed, laboratory experiments indicated that direct photolysis of PbBrCl did not occur with tropospheric solar u.v. light wavelengths. Reactions with sulphur dioxide was negligible, but PbBrCl was slowly converted to Pb(OH)Br by ammonia in water-saturated air, with the main reactions being with sulphates (Biggins and Harrison, 1979). The atmospheric reaction that accounts for the largest quantity of secondary Pb alteration was found to be:

$$2PbBrCl + 2(NH_4)_2SO_4 \longrightarrow PbSO_4.(NH_4)_2SO_4 + PbBrCl.(NH_4)_2BrCl.$$

Apparently, the most commonly recorded atmospheric Pb compound, $PbSO_4.(NH_4)_2SO_4$, is a product of atmospheric reactions (Biggins and Harrison, 1979). This reaction is thought to occur due to the coagulation of primary vehicle exhaust particulates (PbBrCl) approximately 0.015μm in size, which are subject to rapid coagulation processes (Chamberlain *et al.*, 1979) with the ambient sub-micrometer aerosol, in which $(NH_4)_2SO_4$ is often the main component (Harrison and Pio, 1983). $(NH_4)_2SO_4$ is hygroscopic and exists as solution droplets in air at relative humidities > 80% and at lower humidities due to hysteresis effects (Charlson *et al.*, 1978). This enables liquid-phase reactions to occur.

When vehicle exhaust aerosols age, Br is lost to the atmosphere (Harrison and Sturges, 1983). Atmospheric acid sulphates, H_2SO_4 or NH_4HSO_4, react with PbBrCl to produce the loss of Br as HBr:

$$PbBrCl + H_2SO_4 \longrightarrow PbSO_4 + HCl + HBr$$

and

$$6PbBrCl + 2NH_4HSO_4 \longrightarrow PbSO_4 + 2PbBrCl.NH_4Br + \alpha 2PbBrClNH_4Cl + HCl + HBr.$$

All these products have been observed in ambient air samples.

Table 1.2

Tabulated results from a study of speciation of automotive Pb in air, which indicates that Pb compounds are found in areas without an industrial source (Biggins and Harrison, 1979).

Location	Date	Compounds identified
Central Lancaster, A6 road.	May 17-19, 1977	$PbSO_4.(NH_4)_2SO_4$; $PbSO_4$
	January, 30- February 6, 1978	$PbSO_4.(NH_4)_2SO_4$; α-2PbBrCl.NH_4Cl ; $PbBrCl.2NH_4Cl$; NH_4Cl
	June 20- July 7, 1978	$PbSO_4.(NH_4)_2SO_4$; α-2PbBrCl.NH_4Cl ; PbBrCl
	December 1-4, 1978	$PbSO_4.(NH_4)_2SO_4$; α-2PbBrCl.NH_4Cl ; $PbSO_4.(NH_4)_2SO_4$.
Shap, M6 Motorway	September 19-21, 1978	$PbSO_4.(NH_4)_2SO_4$
Red Scar, Preston, M6 Motorway.	October 26-31, 1977	$PbSO_4.(NH_4)_2SO_4$
	November 14-21, 1977	$PbSO_4.(NH_4)_2SO_4$; $PbSO_4.(NH_4)_2BrCl$
	November 21-28, 1977	$PbSO_4.(NH_4)_2SO_4$; $PbBrCl.(NH4)_2BrCl$
Preston, A6 road	August 1-8, 1977	$PbSO_4.(NH_4)_2SO_4$; PbBrCl
	August 8-15, 1977	$PbSO_4.(NH_4)_2SO_4$; $PbSO_4$
	October 4-11, 1977	$PbSO_4.(NH_4)_2SO_4$
London, A5 road	March 21-28, 1977	$PbSO_4.(NH_4)_2SO_4$; $PbSO_4$
	April 4-11, 1978	$PbSO_4.(NH_4)_2SO_4$; $(NH_4)_2SO_4$

1.3.1.2 Lead antiknock additives and PAH emissions

There has been a world-wide decrease in the use of Pb alkyl antiknock additives (Tims, 1983). For example, in the U.K. emissions of Pb from petrol-engined vehicles have decreased from 8,400 tons in 1973 to 7,200 tons in 1984, a 14% decrease (Department of the Environment, 1986). This occurred along with a 25% increase in petrol consumption (Department of the Environment, 1988) and was due to the reduction of the maximum allowable Pb content in petrol of 0.84 gl^{-1} in 1972 to 0.4 gl^{-1} in 1981 and further reductions in 1985 to 0.15 gl^{-1} has reduced to 2,900 tons in 1986, a 55% reduction of total Pb in petrol (Department of the Environment, 1988). The U.K. experience is based upon European Union (EU) Directives. Upto 1985, the majority of E.U countries based their Pb legislation on Directive 78/611/EEC, which sets limits for Pb in petrol at 0.45 gl^{-1} (Council of the European Communities, 1978). In 1985 a new directive (85/210/EEC) required the maximum Pb content of petrol to be reduced to 0.15 gl^{-1} (Council of the European Communities, 1985). In the U.K. the Pb content was reduced from 0.4 to 0.15g l^{-1} in 1986 (Associated Octel, 1987). In order to maintain the rated octane number (RON) of petrol, which was reduced due to the reductions of Pb, the aromatic content of petrol was increased (Camarson and Spencer, 1977 and CANCAWE, 1983) in both Germany and Sweden. This has been shown to increase the polyaromatic hydrocarbon (PAH) content of exhaust (Candeli *et al*, 1983). However, in the U.K. there has not been an increase in PAH vehicle emissions (Baeck, 1992) due to the removal of Pb, because short-chain aliphatic hydrocarbon were increased in petrol and not aromatic hydrocarbons (Table 1.3). However, the recently published Royal Commission report (Royal Commission, 1994) stated that super-unleaded fuel contains aromatic compounds, such as benzene. When these aromatic compounds are not fully combusted they can be emitted from car exhausts into the atmosphere causing a health hazard. One of the recommendations of the Royal Commission report was the removal of super-unleaded petrol from the market place. Thus, it can be seen that the emissions of Pb and PAH are greatly related and this relationship must be taken into account when drafting environmental legislation.

Table 1.3.

Pb and aromatic content of European premium petrol (Associated Octel, 1985, 86, 87 and 88).

*Belgium, Netherlands and Luxembourg.

+ ***Samples taken in winter, all*** other samples taken in summer.

Country	Mean	Pb	content	(g/l)	Mean	aromatic	content	(%Vol).
Year	1984	1985	1986	1987 *	1984	1985	1986	1987
UK	0.4	0.4	0.15	0.15	31.6	29.9	34.3	31+
Germany	0.15	0.15	0.15	0.15	42.6	39.2	41.8	37.8
France	0.4	0.4	0.4	0.4	34	34.4	29.1	31.2
Italy	0.4	0.4	0.4	0.4	29.4	29.5	29.1	29.9
Benelux*	0.4+	0.4	0.15+	0.15	35.4+	33.7	29.5	40.7
Sweden	0.15+	0.15	0.15+	0.15	37.9+	37.9+	39.8+	42.3

1.3.2 Vehicle exhaust particulate size

Approximately 75% of Pb introduced to vehicles as petrol additive is emitted through the exhaust and in particulate form (Huntzicher *et al*, 1975) with the other 25% remaining in the vehicle. The size distribution of Pb particulates emitted from vehicles has been of interest for several years (Hirscher, *et al.*, 1957, Mueller *et al*, 1963, Habibi, 1970 and Ter Haar, 1972). It has been determined that 50% of the Pb is combusted during city driving and that < 5% of that is <1μm in size (Hirschler *et al.*, 1957). Mueller *et al.* (1963) reported that, for a car operating under cruise conditions, 62 to 80% of the exhausted Pb particulates were <2 μm in size. The mean size of the exhausted Pb particulates have been shown to increase with the age of the vehicle (Habibi, 1970 and Ter Haar *et al.*, 1972) for example, at 7,250 miles 1 μm (mass median diameter (MMD), at 16,500 miles 2 μm and at 21,150 miles 4 μm (Habibi, 1970). Some 18% of the Pb combusted in vehicles is emitted as fine (<1 μm) particulates and 11% as coarse (>10 μm) particulates (Ter Haar, *et al.*, 1972). However, over the life-time of a car these proportions alter to about 35% of the Pb burned is emitted as fine particles and 40% as coarse particles (Ter Haar, *et al.*, 1972). Lead is

mostly concentrated in sub-micrometer particulates and consequently when fine particles are released into the atmosphere it may be transported long distances. For instance, anthropogenic Pb has been detected in Antarctic glaciers (Boutron and Patterson, 1986) and in the Arctic atmosphere (Sturges and Barrie, 1989b).

1.3.3 Coal and Oil combustion

Chow and Earl (1972) estimated that coal combustion contributed 920 tons of Pb to the atmosphere in 1968 (0.5% of anthropogenic Pb). They also reported that it was possible to distinguish gasoline and coal Pb by examing its isotopic composition. The isotopic composition of Pb in coal samples does not correlate with the age of plant accumulation or coalification, but the radiogenicity of the Pb in coal is inversely proportional to the Pb concentration. This is due to the gradual accumulation of Pb by coal from its matrix after deposition of the original plant material. The accumulated Pb dilutes the radiogenic Pb components produced by the decay of radioactive uranium and thorium (Chow and Earl, 1970).

1.3.4 Lead smelters

Compounds of Pb emitted by smelting operations are tabulated in Table 1.4 (similar metal phases are found in the internal atmosphere of Zn/Pb smelters). Since industrial hygiene requires workplace air to be vented through stacks outside the smelter, these phases are found in lower concentrations in the atmosphere.

Although Pb smelter emissions account for some 3000 gt^{-1} of metal produced (Pacyna, 1980) they have not been so comprehensively studied as vehicle exhaust and no encompassing theories for their atmospheric chemistry as yet exists. However, the PbS is due to the loss of primary ore minerals by wind. $PbO.PbSO_4$ and $PbSO_4$ are produced as a result of PbS ore sintering (Harrison and Williams, 1983) and are also emitted from Pb blast furnaces (Foster and Lott, 1980). Lead oxide is thought to arise from the oxidation of metallic Pb and salts in the smelting processes, with Pb being formed by the addition of sawdust to molten Pb in the decopperizing process (Harrison *et al.*, 1981).

Table 1.4

Metal phases in stack discharges from Pb smelting operations (Nriagu and Davidson, 1986).

Compound	Stack/Ambient	Reference
PbS	Stack/Ambient	Harrison and Williams (1983); Foster and Lott (1980)
$PbSO_4$	Stack/Ambient	Harrison and Williams (1983); Foster and Lott (1980)
$PbO.PbSO_4$	Stack/Ambient	Harrison and Williams (1983); Foster and Lott (1980)
β-ZnS	Stack/Ambient	Harrison and Williams (1983)
PbO	Stack	Harrison and Williams (1983);
Pb^0	Stack	Harrison and Williams (1983);
ZnO	Stack	Harrison and Williams (1983); Foster and Lott (1980)
CdO	Stack	Harrison and Williams (1983);

1.4.1 The marine environment

In 1962 Chow and Patterson reported that approximately 40 times more Pb was entering the world's oceans via rivers than was being removed by the oceans during prehistoric times, through rivers in the form of authigenic lead in pelagic sediments. The Pb concentration profiles in open ocean waters was found to be high near the surface and declined to constant values in deep water (Tatsumoto and Patterson, 1963a & 63b, Chow and Patterson, 1966). These effects were attributed to aeolian inputs of Pb from vehicle exhausts. This, coupled with the discovery that the Pb/Si ratios in dusts of Greenland snows were found to have increased 300-fold in the past 3,000 years (Murozumi *et al.*, 1969) indicated that anthropogenic Pb pollution was world-wide.

However, in 1974 Patterson discovered that earlier results (Tatsumoto and Patterson, 1963a & 1963b, Chow and Patterson, 1966) were in error. This was due to contamination originating from a Pb aura surrounding the ship and hydrowire, the sampling apparatus. This contamination led to artificially high concentrations of Pb recorded within the oceans.

New Pb concentration profiles of the North Atlantic and North Pacific waters indicated surface maxima and deep water minima (Schaule and Patterson, 1981 & 1982).

Schaule and Patterson (1981 &1982) inferred from North Atlantic and Pacific Pb concentration profiles that Pb had a residence time of several years in surface waters, approximately 20 years in the thermocline and approximately 80 years in deep waters. The North Atlantic surface waters were found to be more contaminated than the North Pacific surface waters. This reflects the different aeolian flux inputs of industrial Pb. It was concluded that Pb contamination effects in the oceans of the Southern hemisphere would not be as great as in the Northern hemisphere, where most Pb emissions occur. Generally, the higher Pb concentrations in the upper waters were attributed to recent aeolian inputs of industrial Pb. Schaule and Patterson also proposed that a 'switchover' from principally fluvial inputs of Pb to the oceans in earlier times to principally aeolian inputs of Pb in recent times may have occurred.

Flegal and Patterson (1983) used Pb isotopes to trace the distribution of Pb pollution in Pacific waters. Further seawater studies in the Pacific ocean (Flegal *et al.*, 1984 and 1986), North Atlantic (Hamelin *et al.*, 1989) and the Sargasso Sea (Shen and Boyle, 1987 and 1988) have indicated that Pb isotopes are a good tracer for the source of Pb within seawater. For example, Pb isotopes were measured to monitor the decrease of anthropogenic Pb in the Sargasso sea following the phasing out of leaded petrol in the USA.

1.4.2 The sediment record

Marine and lacustrine sediments and polar glacial ice hold a relatively undisturbed record of accumulation of anthropogenic Pb (Chow *et al.*, 1973).

1.4.2.1 Marine and Lacustrine sediments

There is a good sedimentary record of the use of vehicle Pb in the environment (Shirahata, *et al.*, 1980, Ng and Patterson, 1982, Shen and Boyle, 1987). There are several descriptions of the increase in Pb pollution which occurred around 1963 when Missouri

ores started to be used in USA gasoline (Shirahata *et al.*, 1980, Shen and Boyle, 1987). In Europe there is no continuous time record available to date European pollution but British and French sediments indicate that polluted samples are very unradiogenic (Petit, 1974, Fachetti *et al.*, 1982, Flament, 1985, Hamilton and Clifton, 1979, Elabz-Poulichet *et al.*, 1984). The difference in source of Pb ore used for Pb-alkylation of petrol produces characteristic European and North American signatures, which has been detected in marine sediments (Hamelin *et al.*, 1990).

Lead isotopic signatures have also been used in lacustrine environments to identify sources of pollution. Atmospheric deposition of industrial Pb was found to account for 64% of Pb inputs into Lake Ontario and >90% of Pb input into Lake Superior (Nriagu, 1986). $^{206}Pb/^{207}Pb$ ratios were used to identify and trace industrial Pb inputs to the Great Lakes (Flegal *et al.*, 1989). The principal sources of Pb contamination in the Great Lakes were identified as industrial Pb from Canada and the USA.

1.4.2.2 Ice cores

The discovery of a high Pb/Si ratio in dusts in Greenland (Murozumi *et al.*, 1969) indicated that anthropogenic Pb had spread to remote parts of the globe. This evidence was supported by Ng and Patterson in (1981) who stated that Pb concentrations of approximately 20pg g^{-1} in modern snow compared to prehistoric snow concentrations of 1pg g^{-1} of Pb. This increase has been correlated with the increased discharge of Pb into the atmosphere of the Northern hemisphere by industrial activities (Nriagu, 1978 and 1979). In Greenland, the USA, Eurasia and Canada are the main sources of atmospheric pollution (Wolff, 1990). Rosman *et al.*, (1993) reported that the USA was a significant source of Pb in the 1970's in Greenland snow (Table 1.5). Since then it has declined considerably in importance. This decline mirrors the decrease in the use of leaded petrol in the USA. This confirmed the suggestion of Boutron *et al.*, (1991) that the decline of Pb concentration by a factor of 7.5 in Greenland snow over the past 20 years was due to a decline in the use of leaded petrol.

Table 1.5

The $^{208}Pb/^{207}Pb$ ratios for Greenland snow during the period of 1968 to 1988, indicating that sources of atmospheric Pb are from Eurasia and Canada (Rosman et al., *1993).*

Location						
Year	**1968**	**1972**	**1976**	**1980**	**1984**	**1988**
Greenland snow	1.159	1.180	1.182	1.182	1.164	1.155
USA Aerosols	1.180	1.200	1.210	1.220	1.210	1.200
Eurasia and Canada	1.140	1.140	1.140	1.140	1.140	1.140

In the early 1980s there was much contention as to whether Antarctica had been contaminated by anthropogenic Pb. Boutron and Patterson (1983) contested that the exterior of ice cores were themselves prone to contamination and that Antarctic samples were also prone to contamination prior to analysis as they contain low Pb concentrations. They therefore analysed the centres of ice cores and found Pb concentrations to be 1-5 pg kg^{-1}. This suggests that remote Antarctic locations are not contaminated by industrial Pb and that the Pb originates from natural sources, such as silicate dust, volcanic eruptions and sea spray.

Boutron *et al.*, (1988) found Pb correlated with aluminium (Al) concentrations (a marker of crustal dust input) during the Wisconsin glaciation. This indicated that Pb input was primarily through crustal dust. In fact pre-industrial concentrations of Antarctic Pb in snow have been calculated to be 0.3 to 0.5 pg kg^{-1} (Wolff, 1990) and are thought to originate from crustal and volcanic emissions. Present day values of Antarctic Pb in snow range from 2 to 7 pg kg^{-1} (Wolff and Peel, 1985, Dick, 1987 and Boutron and Patterson, 1986). These values suggest that Pb in Antarctic snow has increased through anthropogenic inputs. However, it has been suggested that some of the higher values are as a result of local contamination by research stations (Boutron and Patterson, 1986). This has fuelled the debate as to what is an accurate background concentration of Pb in Antarctic snow. This debate is still going on but there appears to be an emerging consensus towards the lower concentration range of approximately 2 pg kg^{-1} (Boutron and Patterson, 1986).

1.4.3 Lead isotopes as atmospheric tracers

Lead isotopic signatures have been used to trace atmospheric pollution (Rabinowitz, 1972; Stukas and Wong, 1981) but have mostly been limited to local or specific sites. The most conclusive identification of Pb transported over distances of 100's to 1,000 km are the studies of Settle and Patterson (1982). They were able to differentiate aerosol Pb collected in the North Pacific between Asian and North American sources. The composition of the atmospheric aerosol at Eniwetok, an island in the North Pacific ocean, showed a strong seasonal change in large-scale wind patterns of the Northern Pacific and the seasonal character of dust storms in desert regions of China (Duce *et al.*, 1980). Settle and Patterson (1982) analysed the $^{206}Pb/^{206}Pb$ ratios in surface waters (1.184) and dry deposits (1.226). Dry deposits were found to originate from particles transported from land. During the dry season, when silicate dust concentrations were highest, the $^{206}Pb/^{207}Pb$ ratio was similar to the ratio in Pb aerosols emitted from Asia and Japan. However, during the low dust concentration periods, the $^{206}Pb/^{207}Pb$ ratio was similar to that emitted from the USA.

Sturges and Barrie (1987) demonstrated that in eastern North America between 1982 and 1986 Pb sources from the USA and Canada could be clearly distinguished by 'marker' ratios (Table 1.6). The variation of $^{206}Pb/^{207}Pb$ were attributed to the widespread use of organolead anti-knock additives in petrol and to national economic influences in the selection of sources of Pb for these additives (Sturges and Barrie, 1989a and b; Hopper and Barrie, 1988).

Table 1.6

Averaged 'marker' ratios of $^{206}Pb/^{207}Pb$ from Canada and the USA aerosol. Values given as mean ± std (N) (Sturges and Barrie, 1987).

Location	1982 to 1985	n	1986	n
Ontario site 1 USA	1.148 ± 0.007	17	1.153 ± 0.005	11
Ontario site 2 USA	1.212 ± 0.008	25	no data	0
USA East Coast	no data	0	1.196 ± 0.007	9
USA Midwest	no data	0	1.221 ± 0.009	14

Sturges and Barrie (1989a, b) also attempted the use of Pb isotopes as tracers for pollution in the Arctic haze. Their results indicated that the Arctic haze was uniform in composition. However, there was no evidence of sources from American, North Canadian smelters or industrial emissions from the Kola Peninsula in the U.S.S.R. It was suggested that the observed $^{206}Pb/^{207}Pb$ ratios of 1.160 and 1.161 for two Canadian Arctic stations are close to Soviet non-ferrous ore deposits of 1.158. However, East Canadian and European sources could not be totally discounted. There are little data available for Europe. Eastern Canada data for $^{206}Pb/^{207}Pb$ ratios have not been found to be significantly different (1.148) from those observed in the high Arctic. Meteorological evidence indicates that Eurasian emissions are transported more effectively than North American emissions (Barrie, 1986). This evidence suggests that Arctic haze pollutants are mainly from Eurasia. However, this can not be verified with $^{206}Pb/^{207}Pb$ ratios since no of data in Europe of Arctic haze origin has (as yet) been measured.

Hopper *et al* (1991) collected a series of daily atmospheric aerosol samples southern Sweden. Subsequent analysis revealed that the $^{208}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios varied considerably, depending on the origin of air. Five-day back-trajectories were used to classify the samples according to source region: Northwest, Western Europe, East, Eastern Europe, or a combination of two regions. Significant differences in the isotope ratios were found. The region signatures were generally consistent with isotope ratios of Swedish and other European gasolines, and with literature values of the isotope ratios of economically significant lead ores used in Europe. The regional signatures and the observed $^{208}Pb/^{207}Pb$ ratios in the Arctic aerosol samples were compared (Arctic $^{208}Pb/^{207}Pb$ = 1.160 and an average source signature of 1.156). The agreement of $^{208}Pb/^{207}Pb$ ratios indicated that the Arctic $^{208}Pb/^{207}Pb$ signature may be acheived by mixing the $^{208}Pb/^{207}Pb$ isotope signature of the East, Western and Eastern Europe regions.

1.5 Trace elements

Globally, anthropogenic emissions of trace metals exceed natural emissions of several trace elements. Regionally, in densely populated areas, anthropogenic emissions of metals are the dominant contributors. This is indicated by the ambient concentration of trace elements in source regions which are orders of magnitudes higher than in remote areas.

1.5.1 Anthropogenic trace element sources

The anthropogenic sources of the trace elements chosen for this study exceed emissions from natural sources. The element choosen were aluminium (Al), arsenic (As), barium (Ba), carbon (C), chromium (Cr), cobalt (Co), copper (Cu), magnesium (Mg), manganese (Mn), lead (Pb), antimony (Sb), vanadium (V) and zinc (Zn).

There are 6 main anthropogenic trace element sources:

1. Fuel combustion
2. Vehicle emissions
3. Non-ferrous metal manufacture
4. Iron, steel and ferroalloy plants and foundries
5. Refuse incinerators
6. Cement production.

1.5.1.1 Fuel combustion

There are many forms of fuel combustion, which can be divided into:

a. External combustion, for example, coal, oil and wood.

b. Internal combustion.

1.5.1.2 Coal combustion

The behaviour of trace elements during coal combustion is dependent upon 4 factors:

1. The affinity of the elements for coal mineral matter
2. Physio-chemical properties of elements and their original concentration in the coal
3. Combustion conditions
4. Emission control devices within the power plant.

Elements in coal may have a high organic or inorganic affinity (Goldschmidt, 1935). For example, the sulphide-forming elements and sulphur are found in the inorganic fractions. The trace elements' affinity for pure coal and mineral matter affects the trace element emissions during coal combustion. This is because the organic affinity is responsible for the element concentrations and the chemical form of pollutants released (Nriagu and Davidson, 1986).

Trace element emissions are dependent upon the combustion conditions such as temperatures, heating rate, exposure time at elevated temperatures and the surrounding environment of either oxidising or reducing conditions. The volatile species in coal are evaporated in the boiler and recondensed as sub-micron aerosol particles or on the surface of ash particles as the flue gas cools in the connective sections (Flagan and Friedlander, 1976; Kaakinen, 1979; Davison *et al.*, 1974; Pacyna, 1980). Therefore, the higher the temperature in the boiler, the larger the emission factors of volatile elements. The concentrations of chalcophiles, such as Pb and Zn, increase markedly with decreasing particle size, while lithophiles show little or no enrichment with decreasing particle size. The other elements such as Cr, Cu, Ni and V display an intermediate behaviour.

Table 1.7

The emission concentrations of trace elements from coal-fired power plants using bituminous coal (Pacyna, 1986).

Element	Cyclone (μgMJ^{-1})	Stoker (μgMJ^{-1})	Pulverised (μgMJ^{-1})
As	24	28	16
Cd	7.3	8.7	5.1
Co	44	51	25
Cr	120	200	85
Cu	94	164	63
Mn	102	186	70
Mo	31	42	19
Pb	85	128	55
V	84	162	58
Zn	119	191	79

Up to 80% of the ash from pulverised coal fire becomes entrained in the flue gases due to the burning of pulverised coal in suspension. However, in cyclone furnaces only 20 to 30% of total ash is entrained in the fly ash (Bobcock and Wilcox Corp., 1972). Therefore, the particle size distribution within stack dust differs from one boiler design to another. The type of fly ash control system and its efficiency are obvious influences in trace element emission. Coal-fired power plants usually have either electrostatic precipitators (ESP) or wet scrubbers installed. In the UK coal plants that have ESP and Venturi wet scrubbers installed for particle abatement preceding the stack have generally less than 1% of the total trace elements of less than 2 μm in size emitted into the environment (Table 1.7).

1.5.1.3 Oil

The trace element emission during oil combustion depends upon 3 main factors:

1. Element concentration in crude oils
2. Physiochemical properties of trace elements
3. Combustion conditions.

The concentration of trace element within crude oils varies widely with and within each oil field. But generally, the heavier the crude oil, the more metal present. For example, V

concentration in Venezuelan crude oil in Boscan is 1,400ppm (the highest V content in the world) compared to 108ppm in Pilon field also in Venezuela (Table 1.8).

Table 1.8

Trace metal concentration ranges of crude oils (Pacyma, 1986).

values estimated from Zn content

Metal	Concentration Range (ppm)
As	0.0024 -1.63
Cd	0.03 *
Co	0.0027 - 14.5
Cr	0.0016 - 0.729
Cu	0.03 - 12.0
Hg	0.014 - 30.0
Mn	0.021 - 3.1
Mo	0.008 - 7.85
Ni	0.2 - 345.0
Pb	0.001 - 0.31
Sb	0.051 - 0.3
Se	0.009 - 1.40
V	0.07 - 1400.0
Zn	0.1 - 86.0

It is thought that up to 90% of the metals are concentrated into the heavy distillate residual fuel oils, asphalts and the liquid and solid waste streams (Smith *et al.*, 1975). The majority of potentially hazardous trace metals are discharged by combustion of residual oil.

The concentration of silicon dioxide and vanadium pentoxide remain constant for combustion temperatures in the range of 500 - 1800K. Nickel emerges at 1800K as an oxide and as a sulphate at lower temperatures. Other metals form sulphates at higher temperatures. As sulphate concentration increases, fewer sulphates are formed. Conversely, at lower temperatures there are more metal sulphates and less SO_2. The sulphur content of crude oil affects the trace element emissions during combustion. This is due to SO_3 adsorption which causes an increase in particulate formation. The stack emission trace element concentration will also depend upon the efficiency of combustion and the deposition of metals within the boiler. Poor mixing, low flame temperatures and short residence time in the combustion zone all result in larger particles with a higher content of combustible matter and higher particulate loadings (Smith, 1962). Pressure also

has a bearing on the particulate size. For example, low pressure atomisation in the burner produces larger fly ash particles and high particulate loading. Pacyma (1986) took all the parameters discussed into account and calculated the emissions of trace elements for European oil-fired power plants (Table 1.9).

Table 1.9

Emission factors of trace elements for the European oil-fired power plants (Pacyma, 1986). The emission factors were calculated for oil containing 1% sulphur.

Element	Emission Factor (μgMJ^{-1})
As	24
Cd	12
Co	130
Cr	43
Cu	174
Mn	41
Mo	28
Ni	1020
Pb	126
Se	18
V	3700
Zn	89

1.5.1.4 Wood combustion

The combustion of wood is still the largest biomass energy source used in many parts of the world and this has many environmental repercussions from deforestation in Asia to increasing greenhouse gases, such as CO_2. However, in the developed countries this is no longer true. Wood burning stoves and fireplaces are the main sources of emissions from residential wood combustion. Particulate emissions are related to inefficient combustion and vary due to the type and amount of fuel burned, fuel moisture, type of stove and draft setting. Table 1.10 indicates the emission factors of trace elements from wood combustion (Nriagu, 1979 and Walsh *et al.*, 1979).

Table 1.10

The emission factors of trace elements from wood combustion indicate that wood stoves and fireplaces vary in trace element emissions (Nriagu and Davidson, 1986).

Element	Wood stove (gt^{-1} wood)	Fireplace (gt^{-1} wood)
Cd	0.3	0.2
Ni	4.7	3.1
Pb	7	4.7
Zn	58	39

1.5.1.5 Vehicles

Gasoline additives such as $PbEt_4$, diesel and jet fuel combustion with metal compound additives for lubricants and wear metals that accumulate in spent lubricants are the largest sources of trace elements from vehicles (Table 1.11). Cass and McRae (1983) reported that in leaded fuels Pb (21.1%[2]) and C (54.5%) are the largest emissions, while in unleaded fuel sulphates (50%) and C (39%) are the largest contributors to vehicle emissions. Brake linings have a high Mg (8.25%) and C (28.3%) content with tyre tread being mainly composed of C (87%) and Zn (1%). Road composite[3] is high in C content (56.2%), Mg (1.12%), Pb (12.8%) and sulphates (1.40%). Vehicles are thus responsible for the emission of a wide range of trace elements into the atmosphere (Table 1.12).

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[2] *All percentages quoted are by weight percent.*

[3] *Road composite is defined as the composition of TarMac as defined by the Department of Transport.*

Table 1.11

A selection of lubricant additives (Smith et al.,1975).

Metal	Representative compounds	Function
Cd	Cadmium dithiophosphates	Steam turbine oils
Cr	Chromium salts	Grease additives
Mo	MoS_2-Mo dibutyl dithiocarbamate & phosphate.	Greases, extreme pressure additives.
Ni	Cyclopentadienylnickel complexes	Antiwear agents, carbon deposits, minimisers, lubricants & combustion improvers
Pb	Lead naphthenate	Extreme pressure additive, greases, gear oils.
Sb	Antimony dialkyl dithocarbamates	Antiwear, extreme pressure and antioxidant additives in conventional and low-ash-type automatic crankcase oils, industrial and automative gear oils, greases (<1-3%).
Sn	Organotin compounds	Antiscuffing additive, metal deactivators
Zn	Zinc diorgano dithiophosphates Zinc dithiocarbamates Zinc phenolates	Antioxidant, corrosion inhibitors, antiwear additives, detergent, extreme pressure additives, in crankcase oils, hypoid gear lubricants, greases, aircraft piston-engine oils, turbine oils, automatic transmission fluids, railroad diesel-engine oils, differential and wet-brake lubricants.

Table 1.12

The percentage chemical composition of fine aerosol emissions from highway vehicles in America (Cass and McRae, 1983).

Element	% Petrol	% Unleaded Petrol	% Diesel Engine	% Tyre Tread	% Brake Lining	% Road Composite
Al	0.043	0.12	0.34	-	-	0.074
C	54.5	39.0	70.0	87.0	28.3	56.2
Ca	-	0.17	0.84	-	5.5	0.86
Cu	0.004	0.024	0.73	-	-	0.10
Fe	0.25	0.11	1.32	-	-	0.333
Mg	-	-	-	-	8.25	1.12
Mn	-	0.015	0.027	-	-	0.0039
Na	-	-	0.37	-	-	0.05
Ni	-	0.015	-	-	-	0.0002
Pb	21.1	-	0.095	-	-	12.8
V	-	-	0.01	-	-	0.00136
Zn	0.213	0.08	0.23	1.0	-	0.151
Sulphate	0.213	50.0	4.2	-	-	1.40

1.4.1.6 Non-ferrous metals

World wide, the major non ferrous metals produced are Al, Cu, Ni, Pb and Zn. There are 3 factors which govern the emission of these elements in smelters:

1. Processes used in metal production and efficiency.
2. Concentrations of trace metal in ore.
3. Type and efficiency of pollution control devices.

Primary production involves roasting of ores and low grade ore enrichment (for Cu, Cd, Ni, Pb and Zn) and smelting. Arsenic, Cd, Cu and Mo are almost entirely discharged in the smelting furnace slag, with Ni, Pb, Se, Sb and Zn being discharged by roasters and converters. There are generally two processes in further primary production of Cd and Zn: thermal smelting and electrolytic extraction. It is the roasting, sintering and reducing processes of production that are responsable for the main source of atmospheric emissions of Cd Pb and Zn. The various processes, efficiency and type of pollution control devices employed at each produce differences in emissions.

1.4.1.7 Iron and steel manufacture.

Dust from blast furnaces is the primary source of trace element emissions from Fe works. The emission rates from blast furnaces vary according to the type of ore and efficiency of control devices. For example Zn emission factors vary from 0.3 (Haematite) to 33 gt^{-1} of pig iron (Magnetite), and Mn emission factors 2.9 (Haematite) to 5.8 gt^{1} pig iron (Magnetite), with 99% efficient control devices (Nriagu and Davidson, 1986).

The emission factors of steel works is dependent upon the type of technology used (open-hearth, electric arc and basic oxygen furnaces) and operating practices (Jacko *et al.*, 1977; Rauhunt, 1978). Electric-arc furnaces typically have Pb emission rates of 6.1 to 16.3 gt^{-1} of steel, however, open hearth furnaces only emit Pb concentrations of 1.7 to 3.6 gt^{-1} of steel and Zn concentrations of 8.6 to 24 gt^{-1} (Nriagu and Davidson, 1986).

1.4.1.8 Refuse incineration.

This is the process by which solid waste is combusted. Refuse incineration can be sub-divided into municipal and sewage sludge.

Municipal: Trace element emissions depend upon the ratio of combustible to non-combustible material, the chemical composition of the refuse, combustion temperature and the efficiency of the control devices. Non-combustible materials produce silver (Ag), arsenic (As), cadmium (Cd), chromium (Cr), manganese (Mn), Pb, tin (Sn), and zinc (Zn). Combustible material releases aluminium (Al), barium (Ba), cobalt (Co), iron (Fe), lithium (Li), sodium (Na), nickel (Ni) and antimony (Sb) (Greenberg *et al.*, 1978a; Law and Gordon, 1979).

The control devices in municipal incinerators are similar to those employed in electric power plants. However, the combustion temperatures are considerably higher and these incinerator devices have particular problems in collecting volatile trace elements (Johnson and Burnet, 1978 and Nriagu and Davidson, 1986). Trace element emission factors were calculated (Greenberg *et al.*, 1978; Scott, 1979 and Law and Gordon, 1979) by using a particulate emission factor of 2.2 kg/t of refuse burned (designated from a range of 0.45 to 4 kg/t of refuse) and average values of the trace element concentrations in dust emitted from incinerators with a control device at 85% efficiency (Table 1.13).

Sewage sludge: The atmospheric trace element emissions are dependent upon the amount of metal in the sludge, combustion temperatures, volatility of metals and type of air pollution control devices (Copeland, 1975; Takeda and Hiraoka, 1976; Wall and Farrell, 1979; Greenberg *et al.*, 1981 and Gerstle and Albrinck, 1982). Increasing combustion temperatures is related to the increase of volatile metal content in the flue gas.

Table 1.13

Trace element emission factors and concentrations in dust of municipal incinerators (Nriagu and Davidson, 1986).

Metal	Mean concentration (%)	Emission Factor ($g\ t^{-1}$)
Pb	8.1	17.6
Sn	1.15	25
Zn	12	260

1.4.1.9 Cement production.

Fine dust particles are the main air pollution products of cement production. The feed systems, fuel-firing kiln systems and the clinker-cooling and handling systems are the main units which emit trace element dust. For example grinding mills are most commonly powered by coal, and thus As, Cu, Cd, Mn and Zn are expected in dust emissions. The type of production processes (dry or wet), the fuel used in the grinding mill, the type of fuel-firing system employed and the type of control devices all greatly effect the trace element emissions during cement production.

1.4.2 Natural sources of trace elements

There are large discrepancies between the few literature data available (Table 1.14). This is due to the parameters which govern trace element emissions. For example trace element concentration in rocks, soil and dust. Within this group volcanic eruptions appear to be the most extensively studied. This source is highly variable in its chemical emissions from the same volcano and volcanoes during eruptions and quiescent periods.

Table 1.14

Emissions of trace elements to the atmosphere from natural sources (in ng Kg^{-1} of dust).

Metal	Volcanic Particles[1]	Windblown Dust[2]	Forest Wildfires[3]	Vegetation[4]	Seasalt Sprays[5]
As	300-800	0.5-2.0	0.5-4.4	3.5	0.1-0.6
Cd	30-800	0.002-1.7	0.03-2.0	2.7-36	0.001-0.003
Cu	200-5,400	0.3-52	0.7-47	33-440	0.02-0.2
Ni	200-5,600	0.5-88	1.4-92	21-280	0.01-0.08
Pb	100-9,600	0.4-70	1.1-78	21-280	0.001-0.09
Zn	500-10,500	0.6-110	5-330	125-1,700	0.004-0.03

1. From Lantzy and Mackenzie, 1979; Nriagu, 1979a; Jaworowski *et al.*, 1981; Gordon *et al.*, 1983; Walsh *et al.*, 1979; Arnold *et al.*, 1981; Phelan *et al.*, 1982; Servant, 1982 and Parcyna, 1982.

2. From Lantzy and Mackenzie, 1979; Nriagu, 1979a; Jaworowski *et al.*,1981; Gordon *et al.*, 1983; Parcyna, 1982 and Walsh *et al.*, 1979.

3. From Lantzy and Mackenzie, 1979; Nriagu, 1979a;Parcyna, 1982a and Davidson *et al.*, 1981.

4. From Nriagu, 1979a and Parcyna, 1982.

5. From Nriagu, 1979a; Jaworowski *et al.*, 1981; Gordon *et al.*, 1983; Parcyna, 1982 and Walsh *et al.*, 1979.

1.4.2.1 Volcanic emissions

Volcanic eruptions are a natural source of trace elements in the atmosphere (Table 1.15). It has been estimated that volcanoes produce 25×10^6 tons of fine particles of radius <20 μm per year (SIMC, 1976). This represents 1 to 20% of the total estimated natural aerosol production. The volcanic dust flux can be greater than that of the continental dust flux regionally, although it is insignificant on a global scale. Mount Etna is an example of a volcano whose emissions have a greater impact on the environment than anthropogenic inputs: Mount Etna extrudes concentrations of Cd, Cu, Hg, Se and Zn which are equal to anthropogenic emissions from countries surrounding the Mediterranean Sea (Buat-Menard and Arnold, 1978).

Table 1.15

Volcanic fluxes to the atmosphere compared with anthropogenic and biogenic sources (Sigurdsson and Laj, 1992).

Trace elements	Volcanic ($x10^6 Kgyr^{-1}$)	Anthropogenic ($x10^6 Kgyr^{-1}$)	Biogenic ($x10^6 Kgyr^{-1}$)
Cu	10	35	3
Mn	45	38	30
Pb	4	332	2
Zn	10	135	8

The greatest volumes of volcanic emissions originates from violently explosive volcanoes which encircle the Pacific Ocean (Cadel, 1975). Basaltic magma is the dominant magma type extruded on the Earth, $20 \times 10^{12} kg\ y^{-1}$, for both hot spots and ocean ridge basaltic volcanism. In comparison the annual mass eruption rate for the dominantly andesitic volcanism of volcanic arcs is $5 \times 10^{12} kg\ yr^{-1}$ (Sigurdsson and Laj, 1992).

Volcanic gas consists primary of H_2O, CO_2, SO_2, HCl and HF with trace quantities of rock-forming and ore-forming elements (Serafimova, 1979). The proportions of water:gas:metals in volcanic gas was calculated to be 1000:77:0.3 (Menyailov and Nikitina, 1980). The emissions of trace elements depends upon the chemical partitioning between the condensed and gaseous phases and the turnover of superficial magma, bringing new non-degassed magma to the surface (Lambert *et al.*, 1986). Volcanic emissions are highly variable in chemical emissions from the same volcano and volcanoes during eruptions and quiescent periods (Table 1.16).

Table 1.16

A comparison of volcanic emission estimates from individual volcanoes.

Volcano	Pb ($x10^{-9}$g/yr)
Mt. St. Helens (USA)	0.06
Poas (Costa Rica)	0.03
Colima (Mexico)	0.23

1.4.2.2 Marine emissions

The sea surface is a source of trace elements. For example, it has been estimated that for the North Atlantic, 5-20% of Cu and Zn in the marine atmosphere originated from the ocean surface (Weisel *et al.*, 1984). The sub-micron ($r =<0.3$ μm) particles consist primarily of non-sea salt sulphate, which result from gas-to-particle conversion of the photo-oxidation products of sulphur-containing gases emitted by the oceans, *e.g.* dimethylsulphide. Particles >5 μm consist mainly of seasalt and the typical concentration of mineral dust in these particles is <5% of the mass of seasalt, except when there is a large input of continental dust. Mineral dust is a highly variable constituent of the marine aerosol. It is transported from semi-arid to desert regions into the marine atmosphere. In clean remote ocean areas, 70% of the mineral dust is associated with particles greater than 1 μm radius (Raemdonck, *et al.*, 1986).

The main components of the aerosols are sea salt, non-sea salt sulphate, mineral dust and to a lesser extent nitrates (Fitzgerald, 1991). The non-sea salt sulphates and nitrates have both a continental and marine source. The concentration of non-sea salt sulphate decreases greatly from coastal region to the remote oceans (Parungo, *et al.*, 1987), but increases markedly over regions of ocean upwelling (Parungo *et al.*, 1986). The production of sea salt aerosol is due to the agitation of the sea surface by the wind. Wind stress on the ocean surface generates air bubbles which burst producing film drops and jet drops (Blanchard and Woodcock, 1957 and Blanchard, 1963). Most film and jet drops have a radius of 10 μm, most film drops 1 μm, and spume drops have a radius >10 μm (Wolff and Peel 1988). Bubbles are numerous in the whitecaps associated with breaking waves, where they are produced by the encapsulation of air into the water by the breaking wave motion. Whitecaps are formed at wind speeds of approximately 3 ms^{-1}, at 10 ms^{-1} approximately 1% of the sea is covered by whitecaps and at 15 ms^{-1} 4% of the surface is covered (Monahan, 1971 and Toba and Chaen, 1973). Each of the bursting bubbles produces 1 to 10 jet drops and up to several hundred smaller film drops, depending on the size of the bubble. After generation the drops become either sea salt particles or sea salt solution droplets. The mechanical disruption of wave crest by the wind at wind speeds > 10 ms^{-1} produces spume

drops (Wang and Street, 1978; Monahan *et al.*, 1986). Both particle concentration and variation with height are strongly dependent upon wind speed.

1.4.2.3 Vegetation emissions

Vegetation can contain and release, either by biological activity or when burnt, large amounts of trace elements, in particular Cd and Zn (Nriagu, 1979; Pacyna, 1986 and Beauford *et al.*, 1977). The content of trace elements in plants is species- and metal-specific, depending on the availability of the metals and the geological origin of the parent material for soil formation. The metal content in plants is also influenced by the age and state of the plant (Siegert *et al.*, 1986). For example the highest Zn content is found in young plants, with Zn concentration being diluted with age (Mugwira and Knezek, 1971).

Schell and Vali (1973) established that vegetation release large numbers of Aitken condensation nuclei (ACN) into the atmosphere. It was also suggested that the ACN play an important part in the formation of atmospheric ice nuclei and the initiation of precipitation. It has also been reported that plants release trace metals into the atmosphere (Beauford *et al.*, 1975). The mechanism of metal release is thought to involve either a vapour phase or sub-micrometer sized particles. Two mechanisms of particle formation have been suggested:

(1) Epicuticular waxes may be metal carriers and fragmentation and loss of wax can occur during rapid leaf expansion.

(2) The production of airborne salt crystals may be associated with water loss during rapid transportation (Nemeryuk, 1970).

These sub-micrometer particles are thought to disperse over large areas and give rise to the metal-enriched particles in remote regions (Pierson *et al.*, 1978; Zoller *et al.*, 1974 and Duce *et al.*, 1975).

1.4.2.4 Crustal emissions

The dry deserts of the world are large dust reservoirs which influence trace elements within the atmosphere. Saharan sand has been found to be transported high into the atmosphere

and can then be widely distributed, *e.g.* over the North Atlantic and onto the American continent (Carlson and Prospero, 1972 and Talbot *et al.*, 1986). Also, Saharan dusts form part of the marine aerosol in the North Atlantic (Schuetz *et al.*, 1981). Work on beach sand in this thesis (Broadhaven) indicates that these dusts are unlikely to be a significant source of trace elments.

As crustal weathering is a major source of trace elements within the environment there have been several methods devised to identify the crustal influences of trace elements. One such method is the determination of enrichment factors (EF). This technique compares the ratio of an element with a reference element in the sample and in the emission pattern of potential source. Iron and Al are commonly used as reference elements for crustal materials (Church *et al.*, 1984; Wolff *et al.*, 1986 and Zoller *et al.*, 1974). Zoller in 1974 determined the EF value for a metal thus;

$$EF_{crust} = \frac{X_{air}/Al_{air}}{X_{crust}/Al_{crust}}$$

where,

X_{air} and Al_{air} = airborne concentrations of any element X and Al

X_{crust} and Al_{crust} = concentrations of any element X and Al in the crust.

If the EF values are near or equal to unity then crustal erosion is the primary source of the element in question. Greater than unity indicates that the sources of the element are not crustal *i.e.* anthropogenic, volcanic, biological methylation, direct sublimation from the crust or aerosol produced at the air-sea interface (Duce *et al.*, 1975). Values less than unity indicate a depletion of the element in comparison with the crust. A similar factor, using Na as a reference, is used to compare element enrichments with respect to seawater.

A large EF in atmospheric particles suggests that there are sources other than seawater or rocks exposed at the land surface or there are low or high-temperature processes that selectively release these metals into the atmosphere from the Earth's surface. Low-temperature processes include the generation of aerosols at the sea surface (Duce *et al.*, 1976) physical or biologically-mediated volatilisation from the Earth's surface (Goldberg,

1976 and Duce *et al.*, 1975) and release of metal-rich particulates from vegetation (Beauford *et al.*, 1975 and 1977). High-temperature processes include volcanism, burning of vegetation, industrial activities and fossil fuel burning.

1.5 Carbon

Carbon[4] was known as a substance in pre-history (charcoal, soot) but, it was not recognised as an element until 1789 when A.L. Lavoisier coined the word carbon, from the Latin *carbo* for charcoal. Carbon occurs both as a free element (graphite and diamond and the allotrope buckminsterfullere C_{60}) and in combined forms, *e.g.* carbonates. An important form of carbon is CO_2, an important constituent of the atmosphere. Carbon in crustal rocks varies substantially, but a typical value is 180 ppm.

Carbonaceous material is a principal component of particulate matter, with C constituting 10 to 20% of aerosol mass (Wolff and Klimisch, 1982; Malissa *et al.*, 1984; Shah *et al.*, 1986). Carbon occurs mainly in aerosols as organic and elemental C. Organic carbon generally accounts for 60 to 90% of the carbon mass in airborne particulate matter (Grosjean, 1984; Shah *et al.*, 1986; Japar *et al.*, 1986; Cadle and Dash, 1988; Valaoras *et al.*, 1988). Some organic compounds have been identified as both mutagenic and carcinogenic, and particulate carbon (also known as carbon black) has been linked with environmental effects such as:

(1) an increase in adsorption of solar radiation which may increase global heating (Chylek *et al.*, 1984; Clarke *et al.*, 1984), (2) a reduction of atmospheric visibility (Pratsinis *et al.*, 1984; Japar *et al.*, 1986) and (3) soiling of buildings (Hamilton and Mansfield, 1991). It is important to realise that carbon black only accounts for some 0.001% of the total carbon cycle and yet this quantity is sufficient to cause concern over possible environmental effects (Wolff and Klimisch, 1982). Its sub-micron mass median diameter (MMD) enables carbon black to penetrate deeply into the lung and be deposited in the pulmonary region where it

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[4]*The word 'carbon' is used when all carbon forms are implied and the symbol 'C' for elemental carbon.*

can slow the clearance mechanisms and provide adsorption sites for toxic pollutants (Heintzenberg and Covert, 1984).

1.5.1 Sources of atmospheric carbonaceous particulates

The increase in the concentration of atmospheric CO_2 has been received with mounting anxiety by some and scepticism by others. Some environmental scientists have associated the increase in CO_2 concentrations with a rise in global temperature, due to the trapping of the Earth's thermal radiation by infrared adsorption in the CO_2 molecules - "the greenhouse effect". However, many scientists argue that climatic change has occurred throughout time and that man has not perturbed the Earth's heat balance system. Some would go further and insist that no such rise in global temperature can be proven to have occurred. This claim may well have some foundation as rapid climatic change over the past 200 years can only be proven if a good standard of accurate temperature records are available. It is argued that such reliable temperature data only dates to the late 18th century and this is an insufficient time scale to assess climatic change as we may only be observing natural variation. Such arguments coupled with the difficulty in obtaining reliable estimates of climatic change have sustained scientific discussion and much public interest. However what is clear is that there has been a perturbation of the C-cycle in the past 30 to 40 years and that it would be prudent to not only conserve resources, minimise waste and improve efficiency but also to collect reliable data on the effects of man on the environment.

1.5.1.1 Anthropogenic

There are three forms of carbon which are manufactured on a large scale and used extensively in industry: coke, carbon black and activated carbon. High temperature carbonisation of coal yields metallurgical coke (a poor graphitized form of C) 92% of which is used in blast furnaces for steel manufacture.

Carbon black (soot) is made by the incomplete combustion of liquid hydrocarbons or natural gas. The world production was 10 million tons per day in 1974. Carbon black has a small particle size (0.02 to 0.3 μm) and 93% is used in the rubber industry to strengthen and

reinforce rubber, *e.g.* car tyres have 3 kg carbon black and truck tyres 9 kg. The other main uses of carbon black are inks (2.6%), paint (0.6%), paper (0.1%) and plastics.

1.5.1.1.1 Activated carbon

Activated carbon is a highly specialised product with a large surface area (typically 300 to 2,000 $m^2 g^{-1}$). Activated carbon is produced by chemical activation or gas activation. Chemical activation involves the mixing or impregnation of a carbonaceous material (sawdust, peat) with oxidising and dehydrating agents when heated to 500 to 900°C, for example, alkali metal hydroxides, carbonates or sulphates (H_2SO_4, H_3PO_4). Gas activation involves the heating of carbonaceous material under low temperature or with steam, CO_2 or flue gas at high temperature (800 to 1,000°C). The main uses of activated C in industry are for decolorizing agents (35%) for the purification of chemicals and gas (25%), in water and waste water treatment (30%) and as a catalyst (10%).

1.5.1.1.2 Hydrocarbons

Carbon is also widely distributed in the form of coal, petroleum and carbonates, where it is immobilised. However, the C-cycle ensures a dynamic equilibrium through natural processes. For example, the CO_2 in the atmosphere (6.7×10^{11}) tonnes is circulated through the biosphere, removed by plant photosynthesis and added by plant and animal respiration, and the decomposition of organic matter. CO_2 is also produced by human activities, notably by the combustion of fossil fuels. There is also considerable exchange between the atmosphere and ocean waters, with CO_2 residence times within the atmosphere of 10 to 15 years, as measured by ^{14}C experiments (Greenwood and Earnshaw, 1984).

1.5.1.1.3 Black Carbon

Black C is often called charcoal, soot or elemental C (Goldberg, 1985) and is highly variable in nature. This is because the term encompasses impure forms of C produced by incomplete combustion, 1320 to 1540°C. Four distinct types of black C have been identified (Medalia and Revin, 1981):

1. Aciniform Carbon

The smallest particles, 20 to 30 μm, formed by the deposition from the gas phase. These particles are spherical and adhere to each other to form straight or branched chains (Wagner, 1978). Aciniform C morphology has been described as cluster of grapes.

2. Carbon spheres

This form has a particle size range of 10 to 100 μm, with a hard, shiny, porous or hollow sphere morphology. These cenospheres are formed from coal and oil combustion, when liquid drops are carbonised without altering their shape.

3. Carbonised wood/coal

These are small fragments of carbonised wood/coal which often maintain the structures of plant or animal parts they originated from. The particles vary in size from microns to cm.

4. Carbonaceous microgels

These are formed when spherical C particles with colloidal dimensions become embedded in organic materials.

Carbon black is mostly used in compounding rubber for vehicle tyres. In the USA approximately 90% of C produced is used in tyres (Medalia, 1974).

1.5.1.1.4 Vehicles

In Europe diesel vehicles have increased in number (Ball, 1984) and as a direct consequence there has been an increase in annual particulate carbon emissions (PCE); on average PCE have increased at a rate of 2×10^{5} $kgyr^{-1}$ from 1971 (Hamilton and Mansfield, 1991). In 1987 diesel emissions accounted for 90% of British, 80% of French and 84% of German PCE emissions (OECD, 1989), and in Vienna diesel fuel engines have been reported to account for 80% of black C aerosols (Puxbaum and Bauman, 1984).

In the USA detailed studies to investigate vehicle contribution to PCE have also been undertaken which indicate that 68% of the airborne particulate mass emitted by vehicles is C (Pierson, 1978). Both the mass and total carbon were strongly correlated to truck traffic.

In contrast the ambient aerosol contained only 20% carbon. Los Angeles is an urban example whose atmosphere in 1980 contained some 60% of black C (Table 1.17). The black C was emitted by vehicles (Cass *et al.*, 1982).

Table 1.17

Sources of black C in Los Angeles atmosphere Jan to Feb 1980 (Cass et al., *1982).*

Source	*%*
Mobile	
Petrol trucks	8
Highway Diesel	30
Diesels: ships, trains etc.	30
Aircraft and other	7
Fugitive	
Tire and brakewear	15
Fugitive combustion	2
Stationary source	
Industrial	8

1.5.1.2 Natural

Carbon is found in both marine and continental aerosols, with the highest concentration in urban areas (Wolff *et al.*, 1982). There is a decreasing gradient for black C from large cities to remote areas (Table 1.18). However, this is not true for organic carbon; this suggests that this is primarily of natural origin. Biomass burning is an important process in the global C-cycle. The burning of plant material may contribute more than 60% of fine carbonaceous material emitted to the troposphere from tropical land areas (Cachier *et al.*, 1985), and 80% of the annually burned biomass is in the tropics (Seiler and Crutzen, 1980). Biomass burning in these areas occurs mainly due to slash and burn agricultural practice. Natural forest fires and other wildfires produce between 0.5 and 9.5 x 10^{12} g yr^{-1} of carbon (Turco *et al.*, 1982). However, recent evidence suggests that a greater proportion of the increase in CO_2 may be due to a decrease in its removal from the atmosphere rather than an in increase in its input as a result of deforestation and other biosphere destruction. Some studies (Cachier *et al.*, 1985; Adams *et al.*, 1977 and Wong, 1978) have suggested that biomass burning in low latitudes is more significant than burning in the middle and high latitudes.

Table 1.18

Black C and organic C in atmospheric particulates (Wolff et al., 1982).

Location	Black C (μgm^{-3})	Organic C (μgm^{-3})
Urban		
New York	13.3	19.8
Denver	5.4	10.4
Suburban		
Warren	3.7	8.6
Pleasanton	3.2	6.4
Rural		
Abberville	1.7	10.8
Lurary	1.7	7.7
Remote		
Pierre	1.1	5.1

Most scientific investigations have not focused on tropical areas. Murphy *et al.* (1970) estimated that managed fires produced <2% of atmospheric carbon particles but wildfires may produce up to 10%. The production of carbon particulates from forest fires is dependent upon the nature of the fuel (Table 1.19) and the temperature of the fire, with temperature and emissions being inversely proportional (Sandberg, 1974). Sandberg found that when the fire temperature doubled the emission factor was reduced by 45%. Thus, to reduce forest fires emissions a hot, fast burn with low content of water-containing materials is required.

Table 1.19

The emission of C particulates from the combustion of Ponderosa pine and Douglas fir (Sandberg, 1974).

Fuel	Emissions (lb/ton)
Ponderosa pine	12.5
Douglas fir (without needles).	6
Douglas fir (with needles).	2.4

The use of domestic firewood is dominant in developing countries. However, there are some urbanised areas in the developed world which are still dominantly firewood burners. For example, the north-east and north-central states of the USA account for 9 to 11% of

the USA's domestic firewood contribution (Lipfert and Dungan, 1983). Wood burning can produce substantial atmospheric particulates. For example 20 to 30% of atmospheric particulates in Denver, Colorado, and 50% in Portland, Oregon are particles produced from wood burning (Dasch, 1982). Furthermore, in areas where residential wood combustion is low the contribution may be high, for example 75% of black C in aerosols from Elverum, Norway (120 km north of Oslo) originated from residential wood burning, which accounts for only 3% of the energy production (Ramdahl *et al.*, 1983).

1.5.2 Transport of carbonaceous particles

There is some controversy over the residence time of particulate carbon (Turco *et al.*, 1982; Ogren and Charlson, 1983). Some workers believe that the residence time in cloud-free air is in the order of months (Turco *et al.*, 1982 and Ogren, 1982) while others believe it to be weeks (Ogren and Charlson, 1983). However, there is agreement that rain scavenges carbon particulates out of the atmosphere. The residence time of carbon particulates are believed to range from 40 days (Turco *et al.*, 1982) to 40 hours (Ogren and Charlson, 1983). Although these estimates of residence times vary greatly, there is little doubt that long-range transport of carbon is possible. Table 1.20 indicates that carbon black is widely spread. An example of long-range C transport is the high concentration of carbon black in Arctic aerosols - 40% of total carbon recorded in Barrow, Alaska. These levels are similar to the values found in Los Angeles and New York.

1.5.2.1 Deposition of carbonaceous particles

The general inertness of carbon black indicates that its removal processes are primarily physical. Carbon black particulates in the atmosphere have a tendency to coagulate and increase in size enhancing the dry deposition process (Charlson and Ogren, 1982). In urban aerosols, where the concentration of both new particles and old particles is high, the lifetime of the particles is thought to be one hour whereas in the upper troposphere it may be days (Goldberg, 1985).

Table 1.20.

Particulate carbon concentration and radius for several environments (Turco et al., 1982).

Environment	Elemental Carbon (μgm^{-3})	Organic Carbon (μgm^{-3})	Particulate Radius (μm)*	References
Urban	1.3-4.2	4.7-11	<1	a,b,c & d
Rural	0.23-3.7	6.4-10.8	-	b,c & d
Continental (remote)	0.17-1.1	5.1	<1	b,c & d
Marine	-	0.2-1.2+	<0.5	e & f
Arctic	0.07-0.6	0.9	-	g,h,d & i

+ May represent total elemental and organic C.

* Size range where approximately 80% of C is found.

a Novakov, 1982; b Wolff *et al.*, 1982; c Mueller *et al.*, 1982; d Heintzenberg, 1982; e Hoffman and Duce, 1972; f Chesslet *et al.*, 1981; g Rosen *et al.*, 1982; h Rhan *et al.*, 1982; i Weschler, 1980.

Atmospheric deposition of carbon is both wet and dry. The importance of the processes is site dependent. Wet deposition however, is thought to have a greater effect. Precipitation removes about $\frac{2}{3}$ of particulate carbon, while dry deposition removes $\frac{1}{3}$. In 1984 Muller calculated that C black had a residence time of 4.5 days and approximately $\frac{2}{3}$ of C black was removed by wet deposition. Wet deposition accounted for 52 to 93% of C black in Seattle, Washington, and 99% in rural sites in Sweden (Ogren, *et al.*, 1984). The median concentration of C black in rainwaters was found to be 60 and 100 μgl^{-1} for Seattle and Sweden respectively. As might be expected, the highest concentration of C black were associated with the lowest rainfalls.

1.5.3 C isotopes

There are two stable isotopes of carbon, the heavy ^{13}C, which constitutes 1% of terrestrial carbon, and the light ^{12}C. The third common isotope, the radioactive ^{14}C, occurs in trace quantities. Carbon isotope composition is conventionally expressed in $\delta^{13}C$ values; the difference between the $^{13}C/^{12}C$ ratio compared to that of the conventional standard. The conventional standard that defines zero permil on the δ scale is a Cretaceous mollusc,

Bellemnitella americana, found in the Peedee Belemnite formation (PDB) in South Carolina, USA. The $\delta^{13}C$ value is expressed as

$$\delta^{13}C\ (‰\ PDB) = \left(\frac{^{13}C/^{12}C\ sample}{^{13}C/^{12}C\ standard} - 1 \right) X\ 1000$$

Thus, an enrichment in ^{13}C relative to the standard is indicated by a positive value and results in 'heavy' carbon. A negative value indicates a depletion of ^{13}C, also called 'light' carbon.

Isotopic variation in carbon occurs because carbon is fractionated by physical and chemical processes such as condensation, evaporation and photosynthesis. The extent of isotope separation can be expressed by the fractionation factor, α, such that

$$\alpha = \frac{R_A}{R_B}$$

where, $R = {}^{13}C/{}^{12}C$

$A = {}^{13}C/{}^{12}C_{Sample}$

$B = {}^{13}C/{}^{12}C_{Standard}$

1.5.3.1 Literature review of C isotopes in the atmosphere

There are still many unanswered questions as to the ultimate biospheric sinks and rates of both the natural and anthropogenic emissions of carbon. Many methods have been employed in attempting to answer this question, such as thermal evolution (Tanner *et al.*, 1982, Cachier *et al.*, 1989), electron microscopy (Russell, 1987), radiocarbon dating (Currie *et al.*, 1983), morphology of particulates (Hamilton and Adie, 1982) and spectrometric methods (Smith *et al.*, 1975). Carbon isotopes have also been used to try and identify the sources, sinks and emission rates of C (Cachier *et al.*, 1989). In this study carbon isotopes have been used to try and identify the sources of carbonaceous particles.

Since the stable isotopic compositions of marine and continental carbonaceous particles were demonstrated to be different (Sackett, 1964), there has been considerable interest in

the use of $\delta^{13}C$ values to distinguish organic sources of C in the atmosphere (Parker, 1971; Chesslet *et al.*, 1981; Cachier *et al.*, 1985 and 1987; Kaplan and Gordon, 1989 and Cachier *et al.*, 1989).

Crustal C is derived from the mantle and thus its bulk isotopic composition is constrained by the isotope mass balance governing the C transfer from this reservoir (Schidlowski, 1988). Mantle C (diamonds, carbonatites and C constituents of mid-ocean basalts) has a typical $\delta^{13}C$ range of -3 to 8 ‰ (Deines and Gold, 1973; Des Marais and Moore, 1984 and Mattey *et al.*, 1984). Schidlowski in 1988 calculated that a reasonable $\delta^{13}C$ value for the primitive mantle, inherited from the solar nebula, would be -5 ‰. If this ratio is then used in Schidlowski's isotope mass balance equation with the long term averages of $\delta^{13}C_{organic}$ (-25 ‰) and $\delta^{13}C_{carbonate}$ (± 0 ‰) being substituted into the equation

$$\delta^{13}C_{prim} = R\,\delta^{13}C_{org} + (1 - R)\,\delta^{13}C_{carb}$$

$$\text{Where } R = \frac{C_{organic}}{(C_{organic} + C_{carbonates})}$$

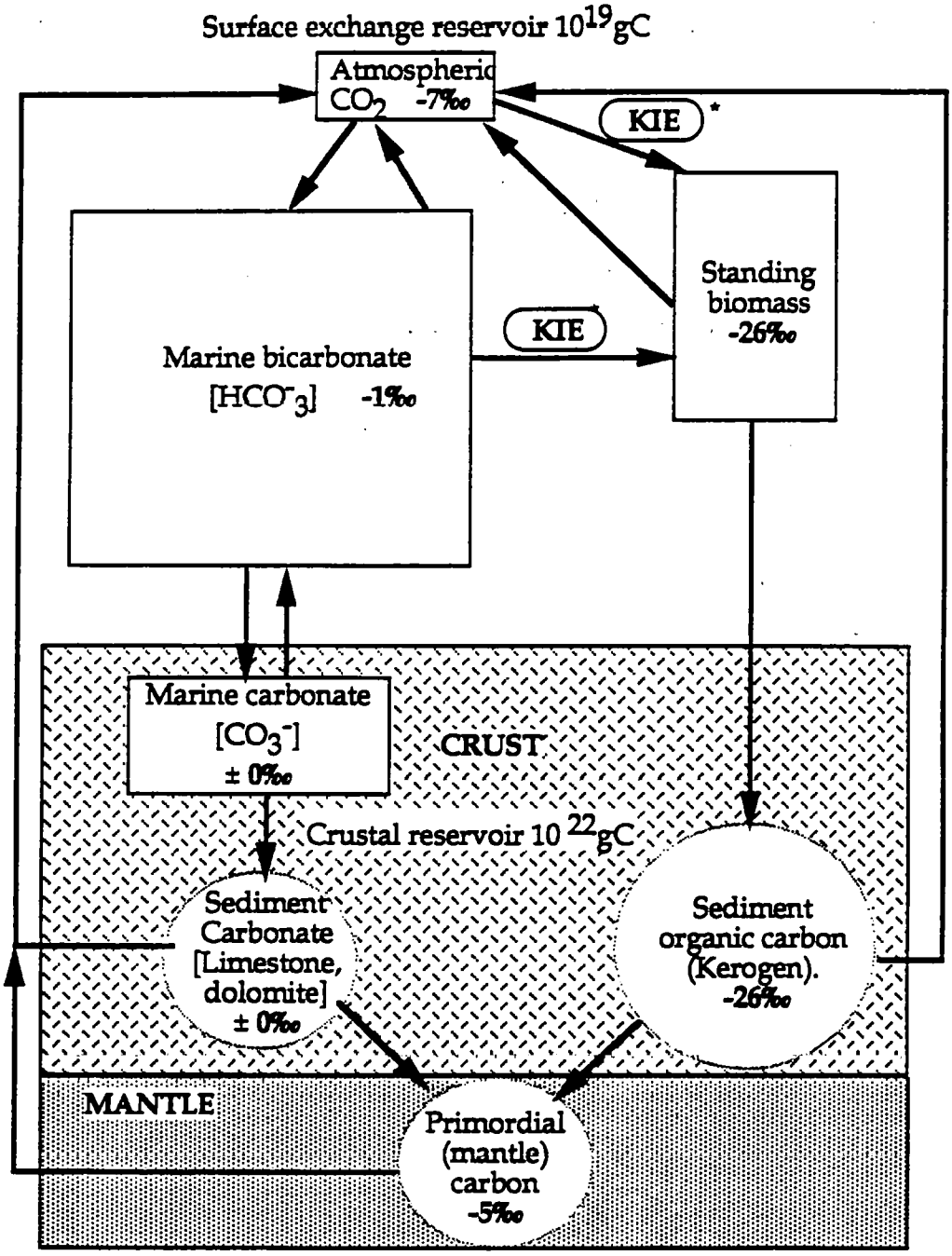
$R = 0.2$

This 0.2 value for R implies that Corganic accounts for 20% and $C_{carbonates}$ for 80% of the total C in the sedimentary reservoir (Figure 1.3).

Carbon isotopic values have proved to be a good tool for estimating qualitatively the relative amounts of marine and continental sources of total particulate C in the marine troposphere (Cachier *et al.*, 1986a). Cachier *et al.* (1985) were able to distinguish between marine and continental sources at Lamto, Ivory Coast by using isotopic signatures: the aerosols in spring were found to be lighter than in the summer, because in the spring C_3 plants were burned (forest mean $\delta^{13}C$ value of -26 ‰) whereas in summer C_4 grasses were burned (savannah mean $\delta^{13}C$ value -12 ‰). This is coupled with the dominant air masses which change with season (spring - Asia and Summer - north. America) to produce distinctive marine and continental signatures.

Cachier *et al.* (1986) reported that the northern and southern hemispheres exhibited different carbon isotopic signatures, suggesting different sources of carbon. It was

essentially all the carbon was derived from marine sources such as planktonic matter and its degradation products. On the other hand the north hemisphere exhibited a greater carbon concentration and a $\delta^{13}C$ (mean) of -25.5 ‰, which suggested a continental source with a combustion component, such as biomass or industrial combustion.



* KIE = The Kinetic Isotopic Effect which produces a preferential accumulation of ^{12}C in organic matter, with much of the heavier ^{13}C retained in marine carbonate.

Figure 1.3.
A flow diagram of the C-cycle indicating the surface, crustal and mantle reservoirs.

1.5.3.2.1 The effect of plants on the $^{13}C/^{13}C$ ratio

Inorganic C is converted into plant material by biochemical pathways (Rankama, 1948). During this process fractionation of the two stable isotopes occurs because of a kinetic effect in the first C-fixing carboxylation reaction, which discriminates against the heavier ^{13}C (Rankama, 1948; Wickmann, 1952; Craig, 1953; Park and Epstein, 1960 and O'Leary, 1981). This has created an imbalance with the ^{13}C being retained in the surface reservoir, mostly as dissolved bicarbonate in seawater (Figure 1.4). As a result the Earth's standing biomass is enriched in light carbon relative to the inorganic C reservoir (Figure 1.4). For example, marine carbonates and bicarbonates have $\delta^{13}C$ values of -2 ‰ to 2 ‰, whereas all the C_3 and C_4 plants have values ranging from -34 to -6 ‰.

Fractionation will vary considerably from plant to plant depending upon which step in the assimilatory pathway is rate controlling (Schidlowski, 1988). Most carbon assimilation is performed by the ribulose 1,5-biphosphate (RuBP) carboxylase reaction, which transfers CO_2 directly to the Calvin cycle, the primary biochemical mechanism for reducing CO_2 to carbohydrate;

$$\mathbf{CO_2 + RuBP \longrightarrow Phosphoglycerate.}$$

The carbohydrate formed from RuBP carboxylase reaction is composed of a 3C skeleton and plants using this reaction are termed C_3 plants. This C_3 pathway is used for photosynthesis by many green plants, eukaryotic algae and most photosynthetic bacteria (Schidlowski, 1988). The C_3 pathway is by far the most significant in terms of CO_2 fixation. It produces a sizeable isotopic effect, with $\delta^{13}C$ values of -26 to 7 ‰ (Figure 1.4). A carboxylation reaction that fixes CO_2 is the use of phosphoenolpyruvate (PEP) carboxylase to produce a C_4 carbohydrate:

$$\mathbf{CO_2/HCO_3^- + PEP/pyruvate \longrightarrow Oxaloacetate}$$

This reaction involves the production of a C_4 skeleton carbohydrate. C_4 plants, anaerobic and facultatively anaerobic bacteria all use this reaction. Crassulacean acid metabolism (CAM) plants are another group of plants which can fix CO_2 by both the RuBP and PEP

carboxylase reactions. This produces $\delta^{13}C$ values between both C_3 and C_4 plants (Figure 1.4).

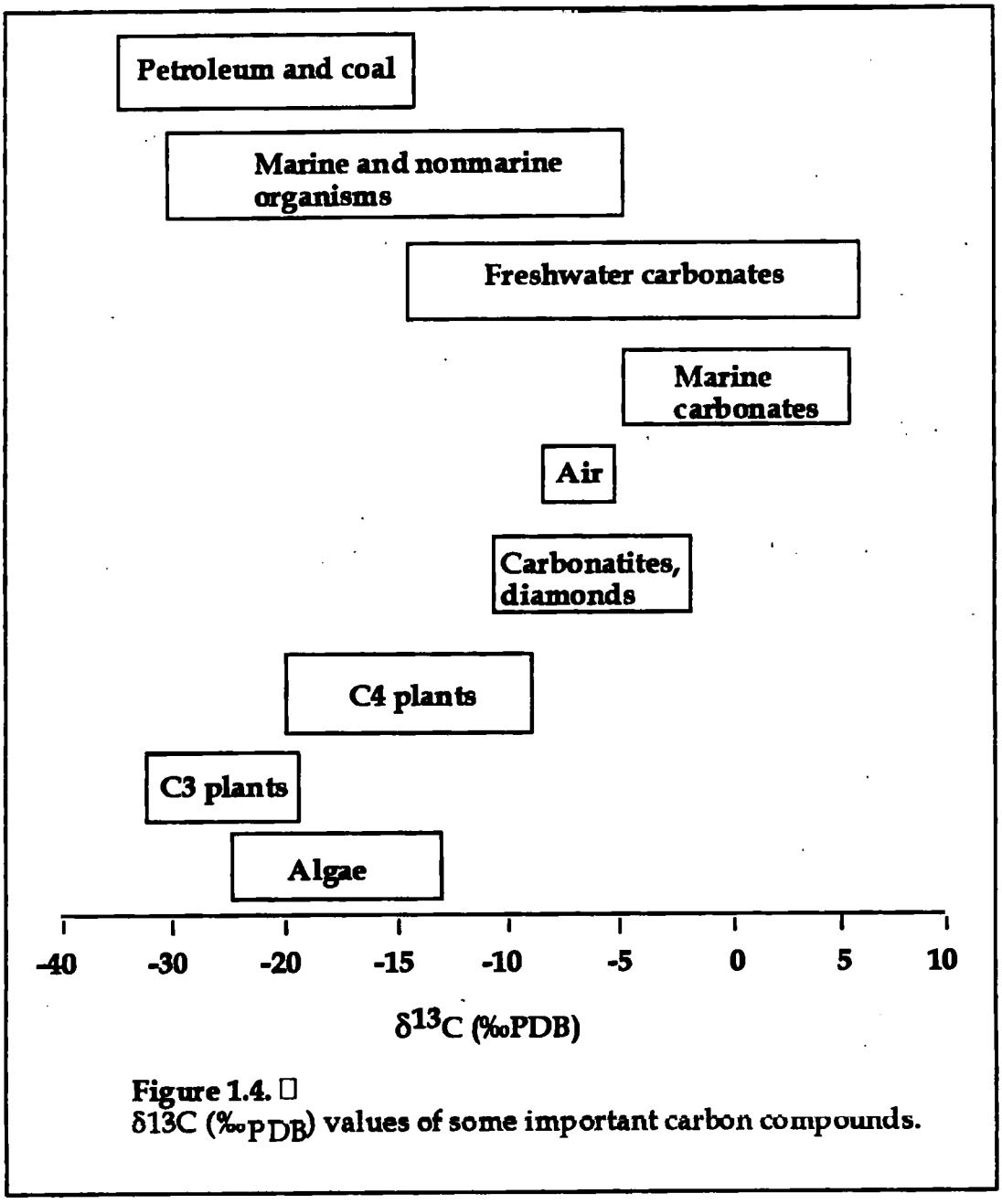


Figure 1.4. □
δ13C (‰PDB) values of some important carbon compounds.

Because there is a biogenic discrimination in favour of ^{12}C, the percentage of ^{13}C atoms in wood is approximately 1% lower than in atmospheric CO_2. When wood is burned, the carbon entering the atmosphere is relatively low in ^{13}C and the change in the $\delta^{13}C$ value is reflected as a year-to-year variations in the isotopic composition of tree rings (Björkström,

1979). An increase in atmospheric ^{12}C from anthropogenic sources would be expected to be indicated by tree-ring analysis but contradictory results have been reported (Jansen, 1962; Dequasie and Grey, 1970; Galimov, 1976 and Farmer and Baxter, 1974a and b). Total wood investigations by Craig (1954), Jansen (1962) and Galimov (1976) indicate a trend to the formation of isotopically heavier wood with lighter wood in the centre of the tree. Jansen (1962) concluded that the $\delta^{13}C$ variations in the tree cross sections are related to differences in the C isotope fractionation during the growth of the trees and this effect may be more significant and mask $\delta^{13}C$ changes in the atmosphere. However, from the analysis of total wood, $\delta^{13}C$ values of atmospheric CO_2 were found to decrease by -2.6 ‰ since the middle of the last century which may be due to the anthropogenic inputs into the atmosphere (Dequasie and Grey, 1970; Freyer and Wiesberg, 1975 and Farmer and Baxter, 1974a). However, a smaller change was found when the tree ring cellulose was examined (Freyer and Wiesberg, 1973 and Rebello and Wagener, 1976). This variation in experimental results is due to the form of carbon analysed. Resin channels permeate the wood tissue and contain organic matter which does not correlate with the age of the wood structure and may be emplaced at different times in the tree history (Freyer and Wiesberg, 1974 and Cain and Suess, 1976). Lignin and cellulose have different $\delta^{13}C$ values and thus their relative abundance will influence the isotopic value if total wood is analysed. Therefore, although it would be expected that the ^{12}C content of atmospheric CO_2 would increase due to anthropogenic emissions, the size and significance of this effect in terms of atmospheric CO_2 concentration changes are still very much a matter of debate (Feyer and Wiesberg, 1974 and Farmer and Baxter, 1974b).

1.6 Research Objectives

The objectives of this thesis are to achieve a better understanding of Pb and C isotopes in aerosols by characterising sources of aerosols. This basic objective was to be achieved by:

(1) establishing if sources of carbon and Pb aerosol particles could be identified in terms of isotope values.

(2) assess if, and to what extent, carbon and Pb isotopic composition and elemental concentration in aerosols are related.

(3) identify any relationships between carbon and Pb particles and local weather conditions, such as rain, wind direction and speed.

(4) establish if there were any temporal variations of the measured elements.

In order to address these research objectives two sample site areas were chosen, Milton Keynes and south Wales, with separate and distinct sampling strategies. The Milton Keynes sampling strategy was designed to establish the main sources of carbon and Pb particles within the Milton Keynes atmosphere and whether weather conditions affected the carbon and Pb isotopic composition of atmospheric particles. Trace element abundance was also to be monitored at this site. The collection of trace element data was to assess if there was an identifiable relationship between the elements monitored and the isotopic values of carbon and Pb. A daily sampling programme which monitored weather conditions (wet and dry temperature, relative humidity, rain, wind direction and speed) was implemented.

In south Wales the primary objective was to perform an isotopic reconnaissance survey in order to ascertain whether Pb and carbon isotopic compositions in aerosol particles varied

along 20 sites of the coast and inland, to establish an overview of carbon and Pb variation in the S. Wales region and to identify main source areas.

The south Wales sample sites were chosen to reflect the main anthropogenic and natural sources of carbon and Pb in the atmosphere, that is rural (soil source), urban (exhaust sources), industrial and marine. Thus the south Wales sampling strategy was primarily designed in order to:

(1) establish if the carbon and Pb isotopic values of aerosols varied along the coastline and inland.

(2) if a variation of aerosol isotopic values was found, to then establish the major sources of atmospheric carbon and Pb particles and to assess if weather conditions affected these sources.

(3) establish if the isotopic values of aerosol are due to single or mixed source values.

(4) if such mixing process existed to assess its importance in respect to carbon and Pb atmospheric particle sources and whether this process was associated with weather conditions, such as increased atmospheric turbulence.

Chapter 2

Sample collection and methodology

2.0 Site descriptions

Aerosol samples were taken from two principal sites, Milton Keynes and south Wales. The Milton Keynes site was chosen as a convenient urban site to identify any concentration and isotopic relationships with weather conditions. The south Wales sampling sites were chosen to establish and characterise Pb and carbon source areas. Five main sites were chosen in order to characterise marine, urban, industrial and rural areas (Figure 2.0).

2.1 Milton Keynes

Milton Keynes is a mainly residential city with some light industry, situated approximately 70 km north of London. Milton Keynes is sandwiched in between the M1 motorway to the north-east and the A5 trunk road running along the south-west. These two main roads, and the mainly dual carriageway urban roads generate most of the city's Pb pollution along linear sources. Point sources of pollution are mainly from small factories and brickworks. All samples were collected at the Open University, which is situated 5 km from the M1 and the A5 (Figure 2.1). All samples at the Open University were taken on top of a three storey building, away from obstructions and most soil or road dust interference.

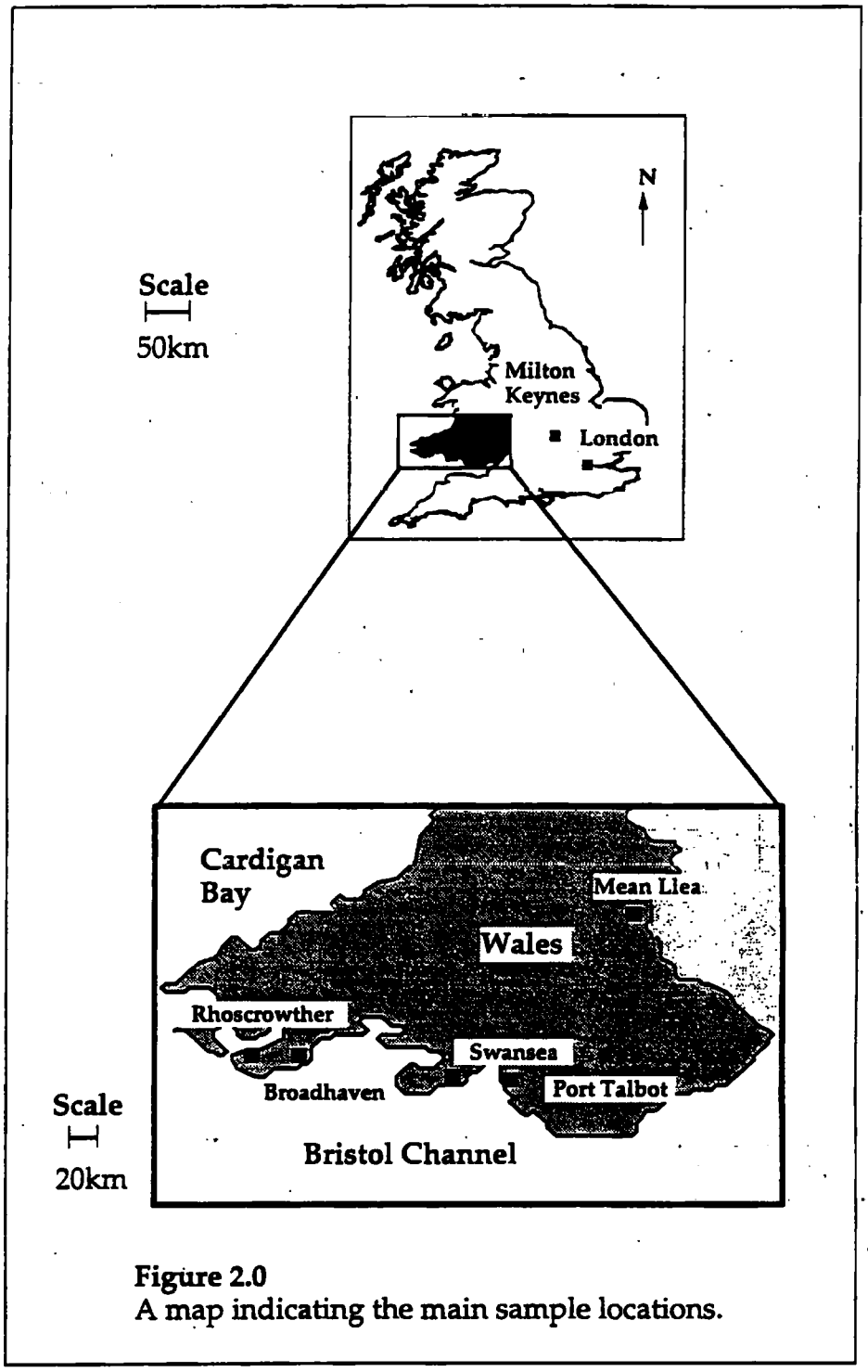


Figure 2.0
A map indicating the main sample locations.

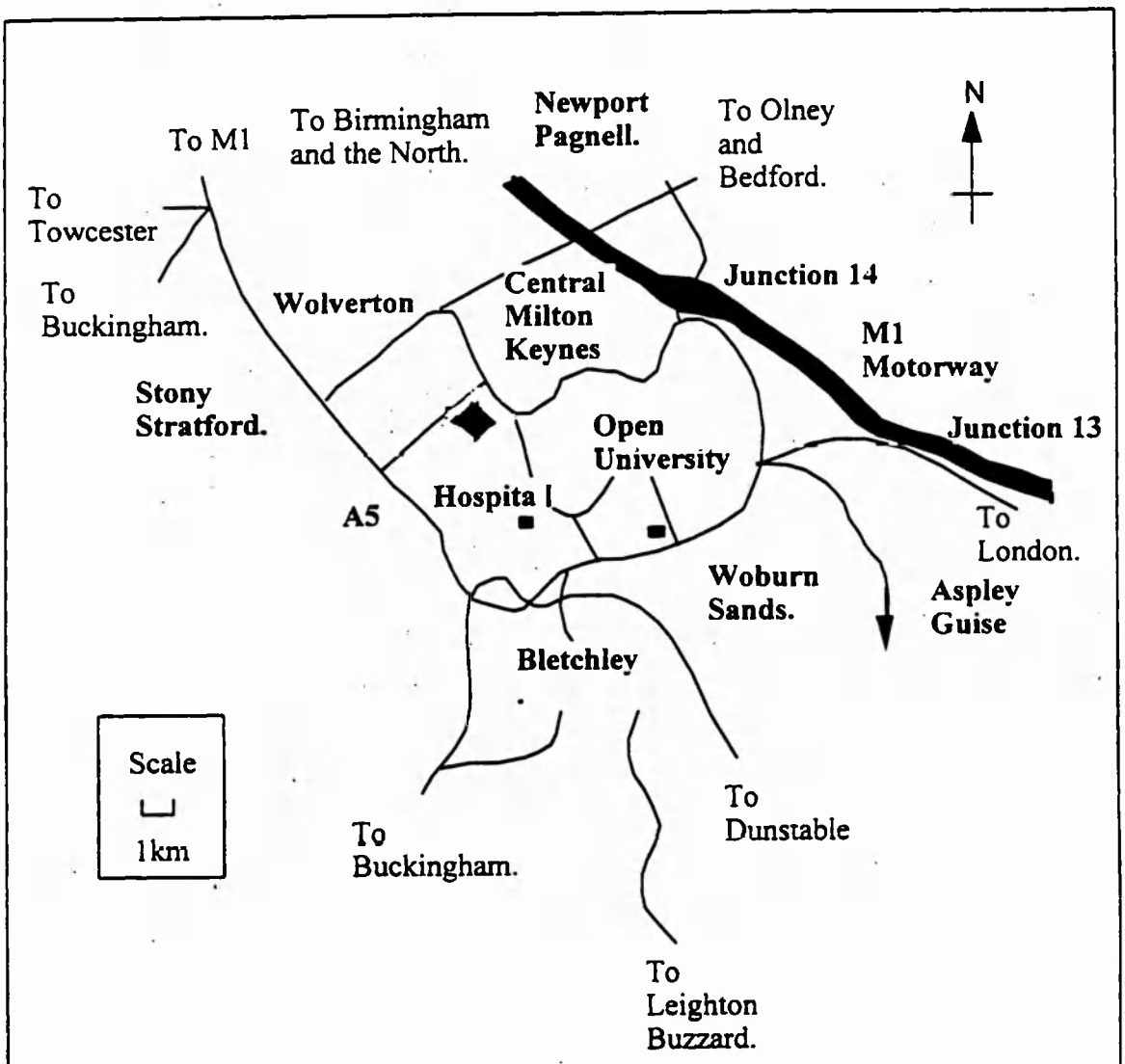


Figure 2.1
A map of Milton Keynes indicating the location of the M1 motorway, main roads and the Open University.

2.3 South Wales

South Wales was chosen as a sampling region because it contains rural, urban, marine and industrial areas within manageable distances and with easy access.

Plate 2.0. Broadhaven (9820 9410) is a secluded sandy bay with steep cliffs on either side, owned by the National Trust.

Plate 2.1.

Rhoscrowther (0240 0234) is a village with a Texaco oil refinery directly at its northern boundary situated some 10 km east of Pembroke.

2.3.1 *Broadhaven*

Broadhaven (9820 9410) is a secluded sandy bay with steep cliffs on either side, owned by the National Trust and frequented by surf boarders (Plate 2.0). Broadhaven is situated 3 km from Bosherton village, some 10 km south of Pembroke (990 012) and is surrounded by Ministry of Defence land used as an Artillery range to the east, rough pasture to the north and west, and is bordered by the sea to the south. All samples were collected on the cliff edge above the beach. This site was chosen to represent a marine site, with little anthropogenic influence.

2.3.2 *Rhoscrowther*

Rhoscrowther (0240 0234) is a village with a Texaco oil refinery directly at its northern boundary situated some 10 km east of Pembroke (Plate 2.1). An oil fired power station lies 3 km to the east of Rhoscrowther, with rough pasture to the south. To the north and west, Rhoscrowther is bordered by the sea. Samples were collected at a layby some 100 m from the village. This site was chosen to represent an industrially influenced marine area.

2.3.3 *Port Talbot*

Port Talbot is a major old industrial port with both heavy and light industry. The heavy industry includes the much reduced British Steel works and a coal fired power station. Port Talbot also has an industrial park which houses the chemical industry including, for example, BP Chemicals. Sampling in Port Talbot was performed some 10 m from the British Steel works boundary at the Port Talbot Fire Station. Port Talbot was chosen to represent an industrial area with predominantly anthropogenic influences.

Plate 2.2.

Swansea is a major light industrial city located on the coast some 15 km north-west of Port Talbot. It also serves as a base for tourists visiting the Gower Peninsular and as a centre for local government administration.

Plate 2.3.

My constant curious companions.

2.3.4 *Swansea*

Swansea is a major light industrial city located on the coast some 15 km north-west of Port Talbot (Plate 2.2). It also serves as a base for tourists visiting the Gower Peninsular and as a centre for local government administration. All samples in Swansea were collected on the promenade. Swansea was chosen to represent an urban area with both industrial and marine influence.

2.3.5 *Mean Llea*

Mean Llea is a remote rural area located 460 m above sea level in the Brecon Beacons (9223 2034). A standing stone is located in this area, some 4.5 m high and 3 m wide. This once was a sacred place for the ancient people that inhabited the area (Plate 2.4). Today this area is used as rough pasture for grazing sheep, with the occasional curious sheep, tourist and the odd soldier on basic survival training (Plate 2.3). Mean Llea was chosen to represent a rural area with little anthropogenic influence.

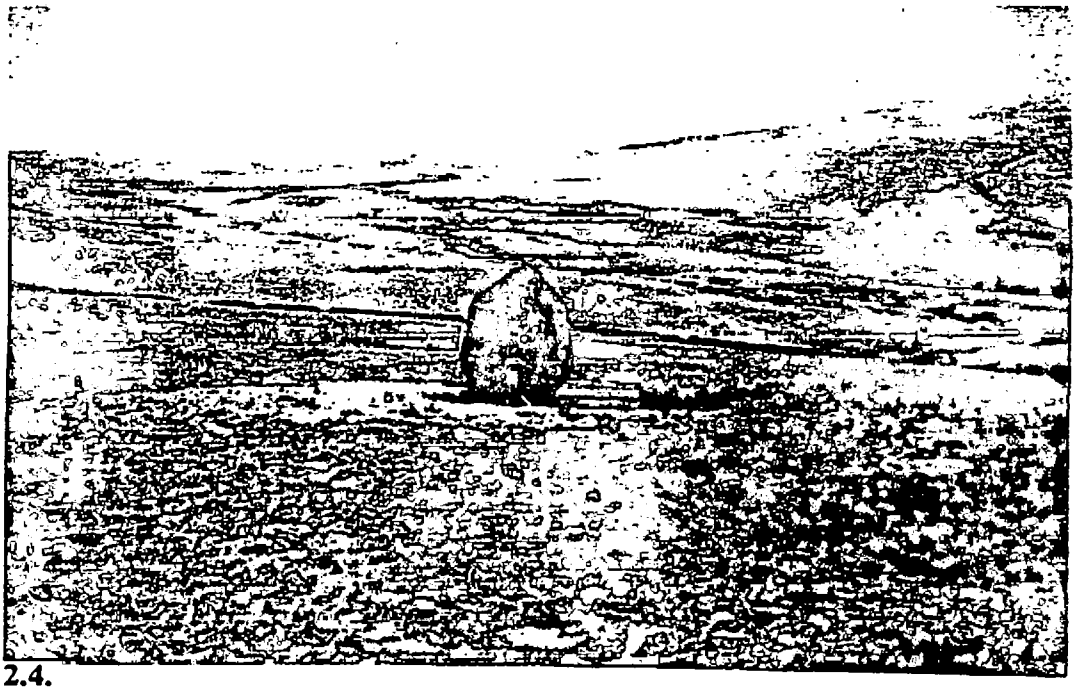


Plate 2.4.

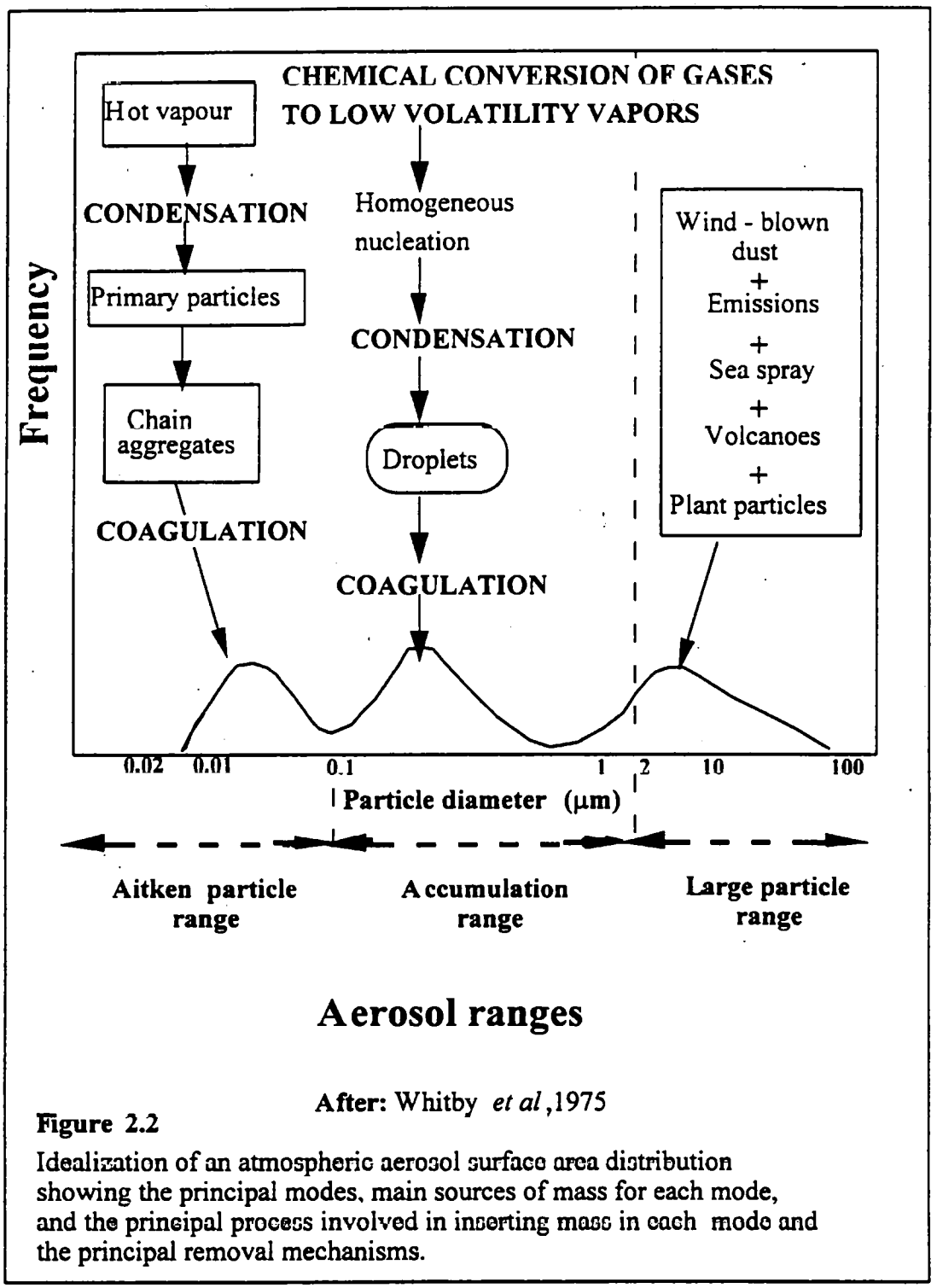
Mean Llea is a remote rural area located 460 m above sea level in the Brecon Beacons (9223 2034). A standing stone is located in this area, some 4.5 m high and 3 m wide. This once was a sacred place for the ancient people that inhabited the area.

2.4 Sampling strategy

The samples taken are essentially spot or snap-shot samples in time. In order to reduce the multiple and varied environmental parameters that have a bearing on aerosol sampling, for example, size, weight and shape of particle, the aerosol particle size was restricted to 5 to 0.5 μm for both carbon and Pb samples. Thus, many particle size-related parameters have been eliminated. Also, Pb particle collection was standardised by a 5 μm millipore primary filter which removed any giant particles before the aerosol was leached by HBr.

2.4.1 Aerosols and particle size

An aerosol is the suspension of particles in a gas. Aerosol particles vary considerably in size, shape, composition and texture (Figure 2.2). Atmospheric aerosols range in size from mm (giant aerosols) to sub-micron (ions) (Figure 2.3). Naturally-produced aerosols may contains wind blown dusts, mechanically-produced plant particles, pollen, volcanic dust and sea salts, all of which are large or giant aerosol particles with high settling velocities. Anthropogenic emissions are generally of micrometer size with a lower settling velocity and are transported further. Whitby *et al.* (1975) indicated that particles in the ambient air are found in 3 distinct size modes (Figure 2.3).



Aerosol ranges

After: Whitby *et al*,1975

Figure 2.2

Idealization of an atmospheric aerosol surface area distribution showing the principal modes, main sources of mass for each mode, and the principal process involved in inserting mass in each mode and the principal removal mechanisms.

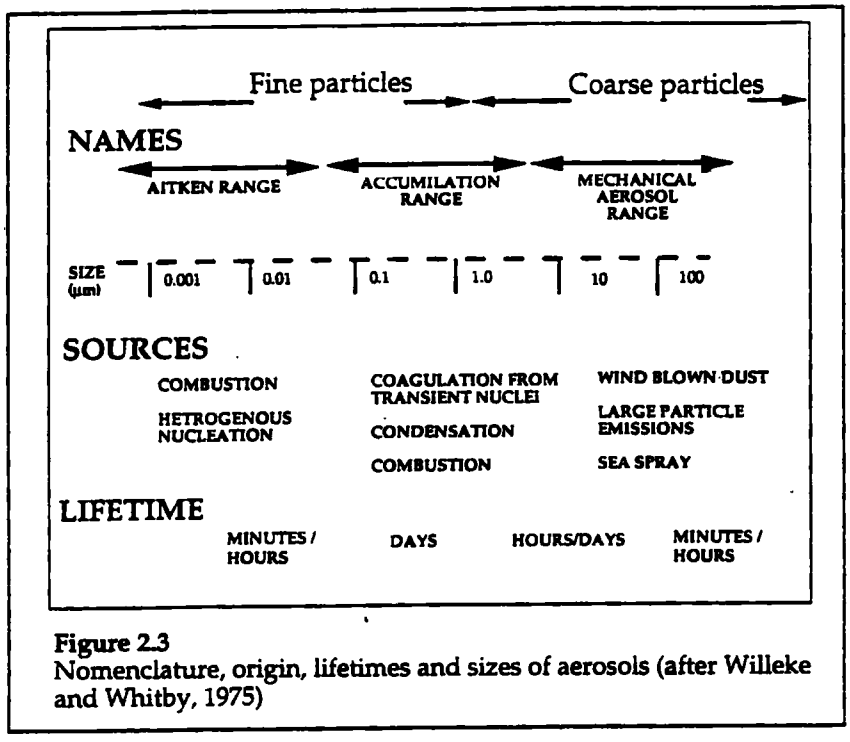


Figure 2.3
Nomenclature, origin, lifetimes and sizes of aerosols (after Willeke and Whitby, 1975)

The ~0.5 to 5 μm particle size was selected for this study for 3 important reasons:

1. Aitken nuclei (particles of diameter <0.01 μm) continually coagulate with one another and as they grow towards 1 μm in size they become more scarce and eventually too few in number to coagulate effectively. However, at this size the particles are still too small to have an appreciable settling rate. Thus, particles of <5 μm accumulate in the atmosphere and do not quickly transfer to the sedimentation mode. So this particle size can be transported long distances, allowing the sampling of particles from a wide and varied region which will alter with seasonal weather regimes. It is this type of particle that is difficult to trace using conventional concentration data.

2. Seasonal differences were also thought to be more prevalent in the accumulation mode, because there is less atmospheric turbulence in the summer and so urban aerosols would be enriched in the accumulation mode particles, which are transported over long distances.

Thus, any seasonal differences in concentration would be more easily recognised in this particle size.

3. At the 0.5 to 5 μm diameter size there is a good distribution of both anthropogenic and natural sources of particles (Figure 2.4). At a larger particle size, the smaller anthropogenic particles would be swamped by larger natural mechanically derived particles, such as sea salt and wax particles and the larger particles would have a disproportionate effect on sampling.

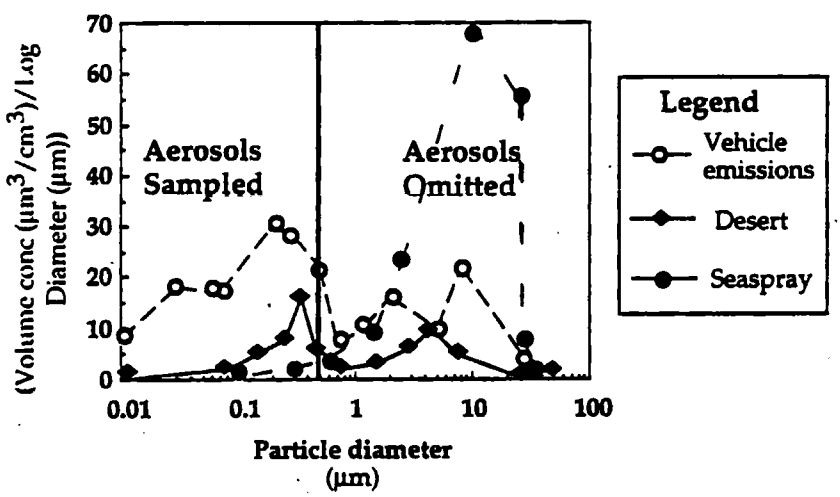


Figure 2.4
A comparison of surface and volume distributions for desert, seaspray and motor vehicle sources (Hidy, 1975) which indicates that at the ≤ 0.5μm diameter particle size range there is a more even distribution of particles from all sources.

2.5 Lead collection and analysis

Air was drawn[1] through the Teflon Pb collecting apparatus[2] (1.2 to 5 m^3) using an SKC™ pump at a rate of 20 litre min^{-1} (Figure 2.5 and Plate 2.5). The aerosol was first passed through a 5 μm millipore filter to remove any large particles and then bubbled through 15 or 30 ml of 1M HBr (depending on the quantity of air being sampled). This procedure traps small particles and leaches Pb from its binding particulates into solution. The HBr sample was then collected in a pre-cleaned Teflon beaker and stored in the dark at room temperature to reduce photo-degradation. Another sample was taken to safeguard against mishap and to monitor sampling consistency.

Soil and sediment samples required an acid digestion procedure to ensure good Pb recovery. Approximately 10 g of the top 5 cm of the soil/sediment were sampled and dried at 100°C for 2 days. The samples were then sieved to produce a homogenous powder. Approximately 0.1 g of soil/sediment was dissolved in a pre-cleaned Teflon bomb by the addition of 1 ml 2 TD 15 ml HNO_3 and 3 ml 2 TD 48% HF. The mixture was then left cold overnight and evaporated. To this evaporated sample a further 2 ml of 2 TD HNO_3 was added and evaporated to dryness. This was repeated until the sample was completly dissolved. To the evaporated sample 2 ml 6M HCl was added and evaporated to dryness. A further 1M HBr was added and left to stand cold overnight. This HBr sample was then taken through the same analysis procedure as the aerosol samples.

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[1] The sampling height was kept at a constant 4 feet from ground level.

[2] The Pb sampling apparatus Teflon components are commercially available and have been adapted to the design in Figure 2.5.

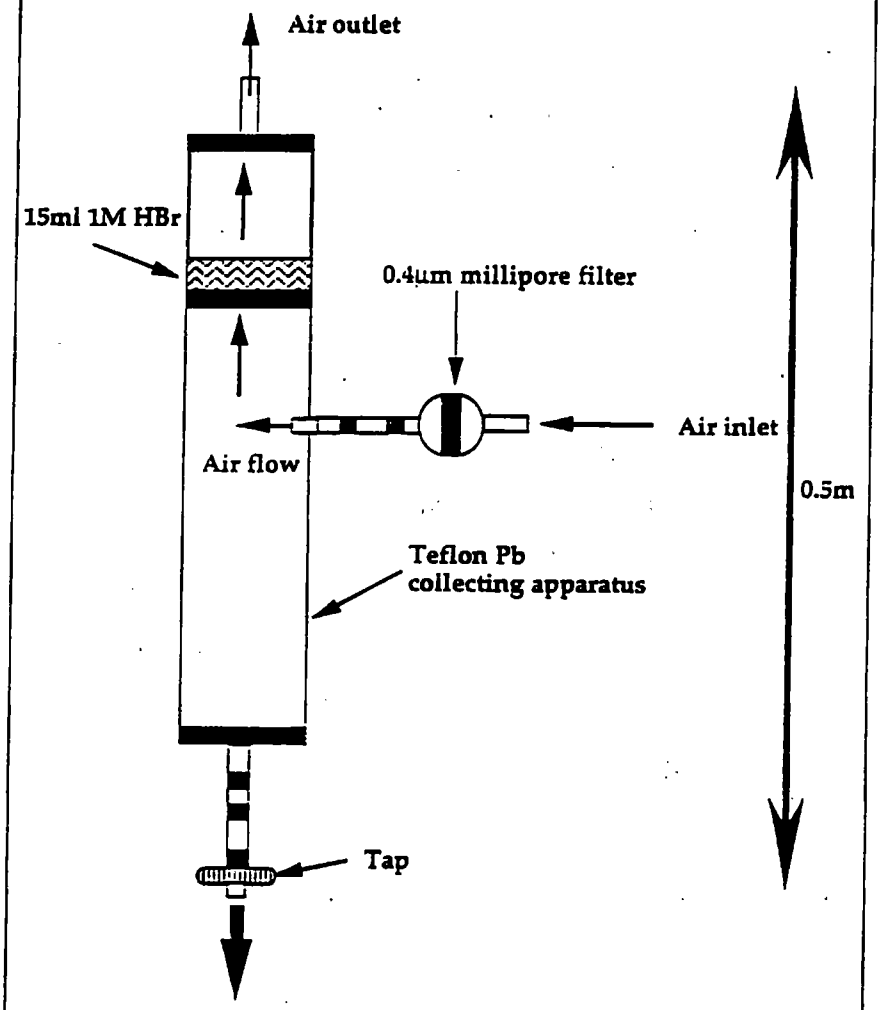

Figure 2.5
Teflon lead collecting apperatus.

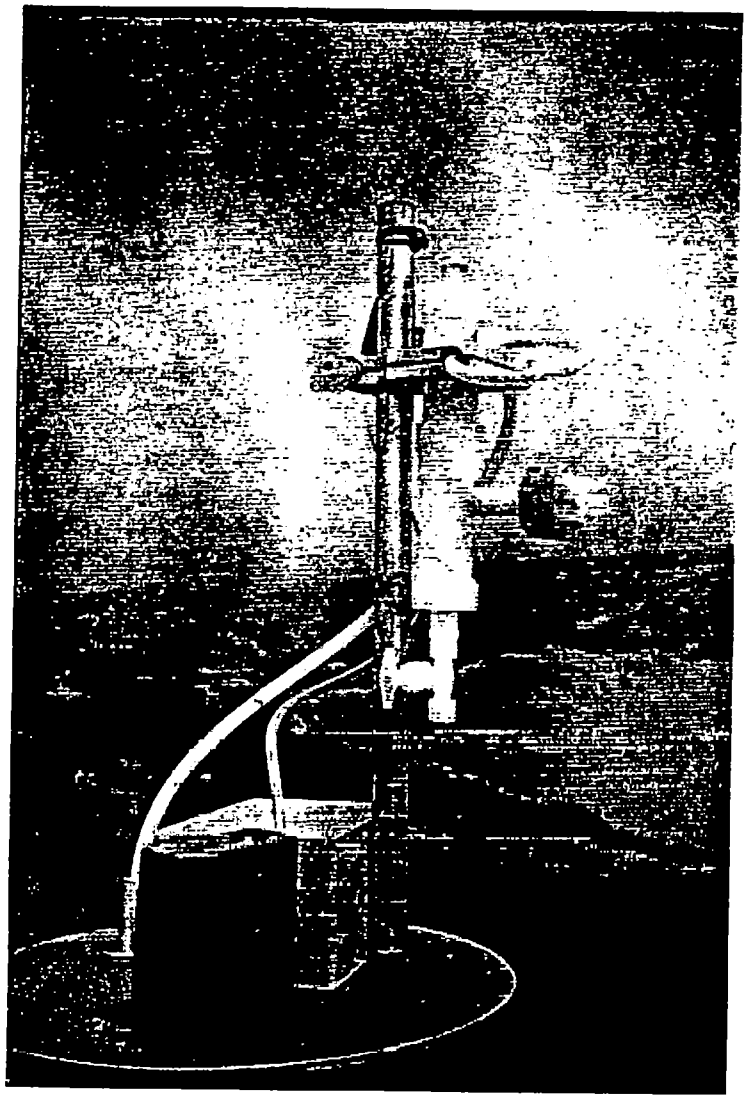

Plate 2.5.

The Teflon Pb collection apparatus.

Petrol samples were once a week for 4 months (September and December, 1992; January and February, 1993). Two brands of petrol (Esso and BP) were collected in Milton Keynes and Swansea. The petrol samples were placed in Teflon containers and placed under and gently heated to evaporate all the volatiles. The Pb was then leached from the residual non-volatiles with 2 ml 1M HBr. This leaching procedure was repeated. The resulting petrol leachate was then prepared and anlaysed in the same manner as the other Pb samples (sections 2.5.1.1 to 2.5.2.1).

Exhaust fumes were collectd by running the Pb collecting apperatus and the cyclone within the same operating conditions as stated in chapter 2 and running the engine for 30 minutes. However, the samples were taken at the exhaust manifold height and approximately 0.5 m from the exhaust manifold. The samples were then prepared and analysed using the method described in (sections 2.5.1.1 to 2.5.2.1).

Several weather parameters were also monitored as part of the sampling strategy; dry and wet temperatures, relative humidity, wind speed and direction and other general weather conditions, such as precipitation type.

2.5.1 Carbon and lead apparatus efficiency

Sampling apparatus efficiency is defined as the difference between the number of particles passing through the samplers limiting stream surface and the actual number of particles reaching the filter (Figure 2.6). The actual number of particles reaching the filter, N_f, is given by

$$N_f = P(N_s+N_r)$$

where,

P = The fractional penetration of particles through the transition section.

N_s[3] = The number of particles passing through the sampling plane (having arrived there directly).

N_r = The number of particles passing through the sampling plane which have undergone impaction and subsequent rebounded from the external surfaces.

Thus, the efficiency of a sampling apparatus, E, is defined as

$$E = \frac{N_f}{N_0} = \frac{P(N_s+N_r)}{N_0}$$

---

[3]*Both N_s and N_r may contain particles that were not included in N_0 but were contained within the sampling apparatus.*

where,

N_O = the 'actual' or 'True' number of particles passing through the incident plane.

This method of assessing sampling apparatus efficiency requires N_O to be known. Unfortunately, in this study N_O could not be calculated because a particle counting apparatus was not available and the concentration values could not be substituted for N_O, as no published data in the $^{2}0.5$ μm size particle range exists for the sampling sites chosen.

If there was fractionation associated with sampling inefficiencies, then the sampling efficiency would become important.

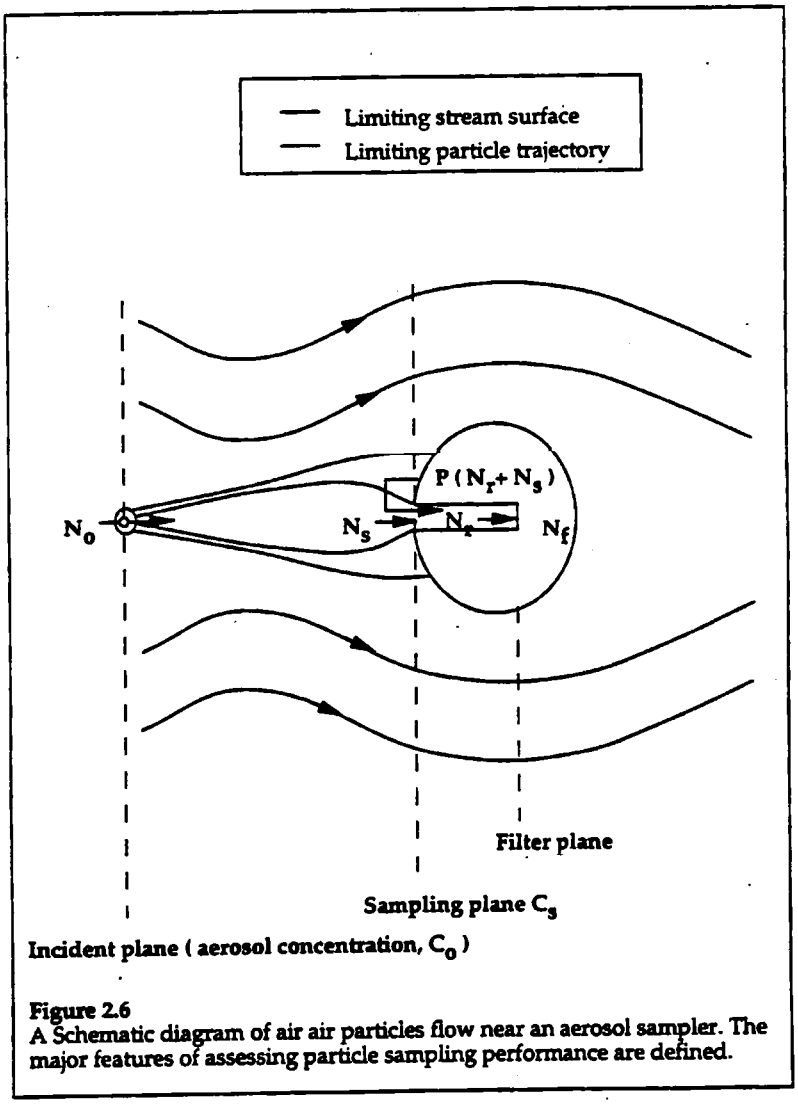

Figure 2.6
A Schematic diagram of air air particles flow near an aerosol sampler. The major features of assessing particle sampling performance are defined.

However, it was assumed that fractionation did not occur. Thus for isotopic composition studies, the apparatus sampling efficiency would not alter the isotopic composition and so for this study it was not considered important. Concentration data however, have to be considered with caution. So, although the actual sampling efficiency in terms of concentration is not known, it would only be of importance if the sampling efficiency were not consistent. Thus, a second set of samples were taken to check for any sampling consistency discrepancies. Sampling inconsistency was defined as the percentage difference between the first and second sample taken, with the assumption that the environmental conditions were equal during both sampling episodes. Thus, consistency was used as a measure of reproducibility. Therefore, apparatus sampling efficiency was not strictly addressed, but sampling **consistency** was monitored. Pb sampling consistency was found to range from 100 to 48% with a mean of 74% (Stdv = 16) (Appendix A(i)).

2.5.1.1 Lead analysis

Before each sample collection and analysis the beakers were cleaned by boiling twice in concentrated HNO_3 and then boiled in Milli-Q-reverse osmosis purified water (R.O. H_2O). The beakers were then dried and sealed with 2 ml HNO_3 and left on a hotplate for one hour. Before use, the beakers were rinsed with Teflon-distilled (TD) H_2O and dried.

The HBr samples were spiked with approximately 0.02 ml ^{206}Pb spike and then evaporated to dryness in a purified air flow in a PTFE pot under a heat lamp. To the residue 0.5 ml of TD 15M HNO_3 was added and placed in a closed beaker on a hotplate in order to dissolve the residue. The HNO_3 was then evaporated and 0.5 ml of 6M HCl was added to dissolve any residue. This was subsequently evaporated to dryness. Finally, the sample was dissolved in 1 ml of 1M HBr and left to stand overnight. The sample was then passed through an anion exchange column.

All of the Pb isotope analyses were performed at the Open University clean-air laboratories. All reagents were TD or twice quartz distilled (QD). All solutions were prepared with R.O H_2O.

2.5.1.2.1 Anion exchange chromatography

The columns were made of 1 ml polypropylene pipette tips with a small Teflon frit in the tip and then stored in hot R.O. H_2O until used. The columns were washed with R.O. H_2O, and two column volumes (CV) of QD 6M HCl. The columns were packed with approximately 15 to 20 µl of Dowex 200-400 mesh anionic resin and columns cleaned with two alternate washes of 1CV 6M TD HCl and 1CV TD H_2O and preconditioned with 0.5 CV 1M HBr. The Pb sample was then added to the column and allowed to elute through the packing. The Pb sample was then washed with 1.5 ml 1M HBr. The Pb was finally collected in the pre-cleaned Teflon beaker, with 2 ml 6M HCl; 3 to 4 drops of TD 15M HNO_3 were added to the collected HCl and evaporated to dryness. The sample was then dissolved in 1M HBr and allowed to stand overnight. This procedure was repeated and 1 µl of H_3PO_4 was added to the collected HCl before the second evaporation, in order to concentrate the Pb into the H_3PO_4 for loading.

2.5.1.2.2 Lead blanks

Blank levels for all reagents used and Total Procedural Blank (TPB) were assessed for every batch of 12 samples. Reagent blanks were measured in order to assess the Pb contamination contribution towards the TPB (Appendix A(ii)). The TPB values ranged from 0.03 to 1.51 ng (mean TPB = 0.673 ng (Stdv = 0.486); this on average represents 1.4% of the sample (Stdv = 1.2). Any samples that exhibited a TPB of >4% were rejected as these would have had an affect on the sample analysis (Appendix A(ii)).

All sample values are quoted as blank corrected values.

2.5.1.2.3 Sample loading

2 µl of silica gel and 1 µl of H_3PO_4 were added to an outgassed single zone refined rhenium filament and evaporated to dryness at 0.8 amps. The sample was then loaded and left to dry at 0.8 amps. Once dry the current was slowly increased to ²1.8 amps, until fuming of H_3PO_4

released the H_3PO_4. The samples were then analysed using Isotope Dilution Mass Spectrometry (IDMS) with a VG54E solid source mass spectrometer.

2.6 Mass Spectrometry

The VG-Isomass 54E solid source mass spectrometer was used to determine both concentration and isotopic abundance on the same sample (Figure 2.7). Natural isotopic variation was taken into account. Samples which ran with a beam intensity on the ^{208}Pb peak of <1 pA were rejected, as intensities less than this resulted in large errors on the ^{204}Pb peak relative to the ^{206}Pb, ^{207}Pb and ^{208}Pb peak measurements. In order to measure mass spectrometer accuracy and precision and to monitor isotopic fractionation a standard (NBS981) was run approximately every 5 samples. The mass fractionation of Pb can be defined by the equation;

$$\mathbf{R = Rm\ (1 + \varepsilon dm)}$$

where,

R= the real value.

Rm = the measured value of the ratio R.

ε = a mass discrimination coefficient per mass unit

For example,

NBS981 based on the recommended values :

$$^{206}Pb/^{204}Pb = 16.937$$

$$^{207}Pb/^{204}Pb = 15.491$$

$$^{208}Pb/^{204}Pb = 36.702.$$

dm= mass difference between the two isotopes of ratio R.

The correction factors for the NBS981 standards measured during the study with the raw data, calculations and fractionation have been assembled in Appendix A(iii).

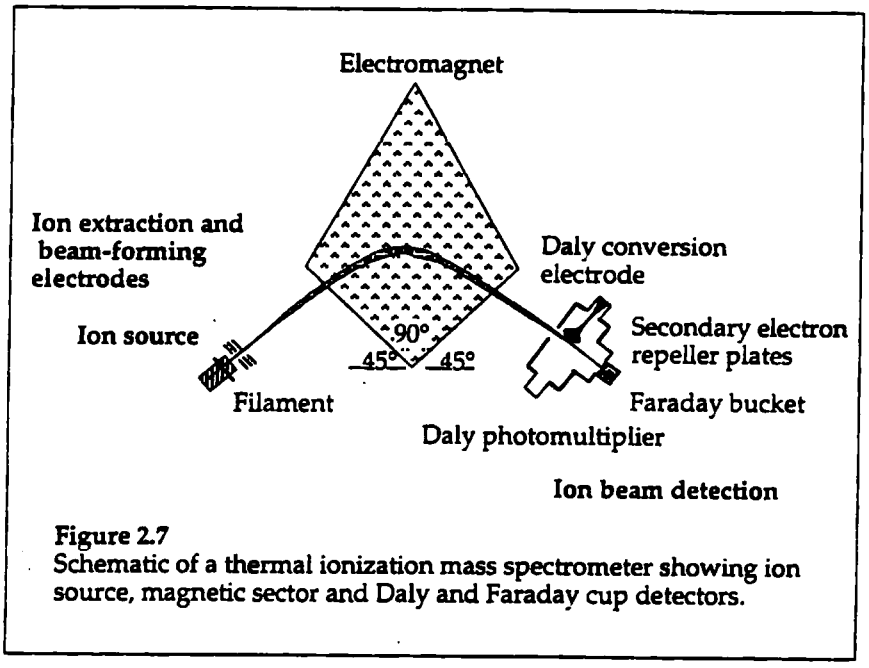

Figure 2.7
Schematic of a thermal ionization mass spectrometer showing ion source, magnetic sector and Daly and Faraday cup detectors.

2.6.1 Isotope dilution mass spectrometry (IDMS)

The principal of IDMS is that a known quantity of a spike isotope, usually a stable isotope with a minor natural abundance (in this case ^{206}Pb) is homogeneously added to the sample. Ratios are then measured with a thermal ionisation mass spectrometer.

2.6.1.1 Sources of error in IDMS

In 1986 Adams stated that there were three main possible sources of IDMS error, this study took these into account when using IDMS;

1. Isotopic fractionation in ion source. This was monitored by regular NBS981 standard checks (Appendix A(iii)).

2. Isotopic variation in nature. This technique assumes that Pb isotopes in the sample have their normal abundances (52% ^{208}Pb, 22% ^{207}Pb, 25% ^{206}Pb and 1% ^{204}Pb). Thus the

analyses were monitored for any variation in natural isotopic ratio abundances and interference ratios were corrected accordingly.

3. Non-equilibrium of the isotope dilution process. This was not a problem in the Pb solution samples because there are no chemical barriers to the homogenisation's of spike and sample.

2.7 Carbon collection and analysis

Carbon particles were collected, on pre-weighed 0.4 μm silicate fibre filters, with the use of a cyclone (Figure 2.8) at 2.5 litre min^{-1} for 2 hrs (as recommended by the manufacturer). The cyclone was pre-cleaned with a 1:1 methanol/toluene solution and then stored in solvent-cleaned Al foil. The cyclone produces an efficient size separation of the larger particles (>1 μm) that are not required for analysis (Figure 2.9). The filters were stored in solvent-cleaned Al foil at -15°C to avoid bacterial growth.

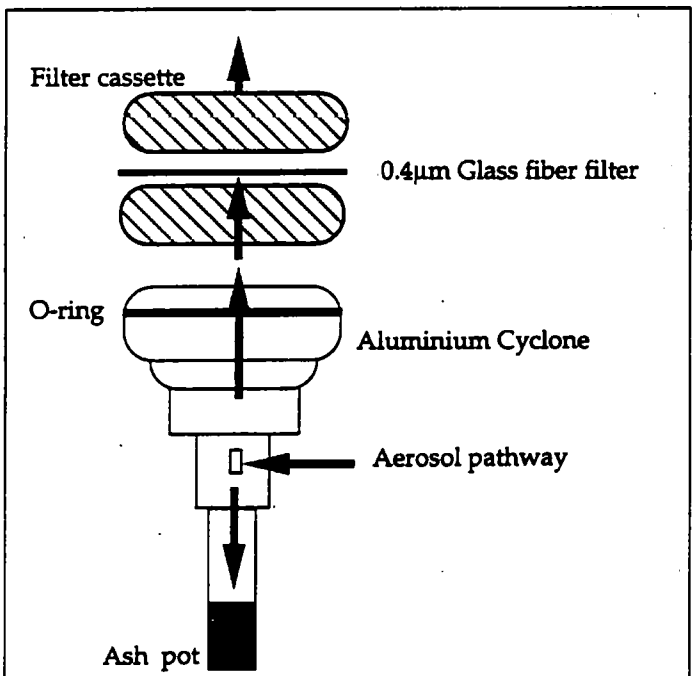

Figure 2.8
A schematic diagram of an aerosol pathway through a cyclone.

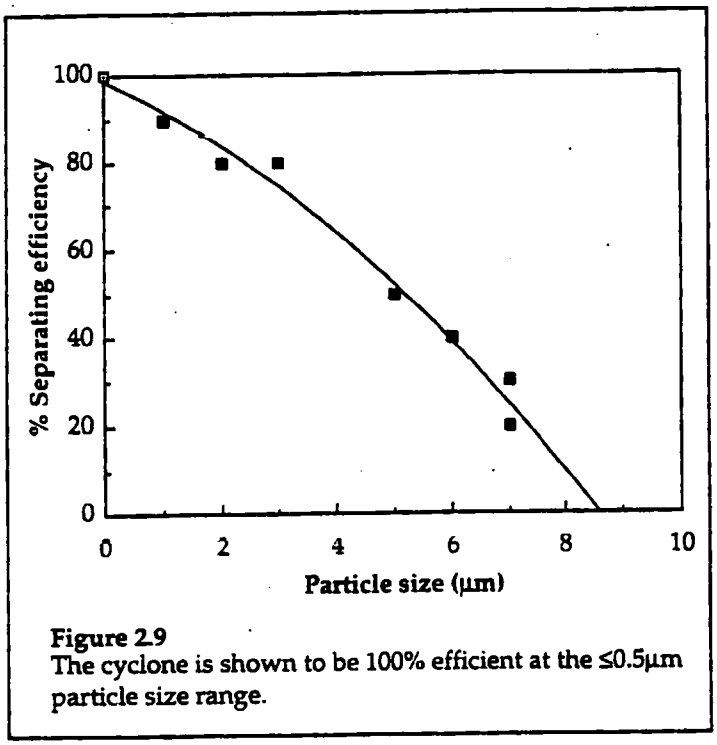

Figure 2.9
The cyclone is shown to be 100% efficient at the ≤0.5µm particle size range.

In order to produce acceptable blank levels four filter preparations were assessed:

Carbon combustion

The silicate fibre filters were placed in a muffle furnace at 450°C for 3 hrs to combust any organics present. The cleaned filters were stored in solvent-cleaned Al foil.

Solvent extraction 1

The silicate fibre filters were placed in 100 ml of a 1:1 mix of toluene/methanol[4] solution and then placed in an ultrasonic bath for 30 mins. The solvent mix was then evaporated overnight in an oven. The cleaned filters were stored in solvent-cleaned Al foil.

---

[4] *All solvents used were of Fissons HPLC grade, 99.8%pure.*

Solvent extraction 2

The silicate fibre filters were placed in 100 ml dichloromethane (DCM) and then placed in an ultrasonic bath for 30 mins. The solvent mix was then evaporated overnight in an oven. The cleaned filters were stored in solvent-cleaned Al foil.

Solvent extraction 3

The silicate fibre filters were placed in 100 ml DCM and then placed in a ultrasonic bath for 60 mins. The solvent mix was then evaporated overnight in an oven and then the filters were placed in a muffle furnace at 450°C for 3 hrs to remove any trapped volatiles within the fibres. The cleaned filters were stored in solvent-cleaned Al foil.

The DCM extraction and filter roasting procedure was found to be the most effective cleaning method, producing the lowest average blank levels of 0.2 mg cm^{-3} (Stdev = 0.05) and so this was chosen as the regular filter cleaning procedure (Figure 2.10). All filters were stored at -15°C and thawed at room temperature before use.

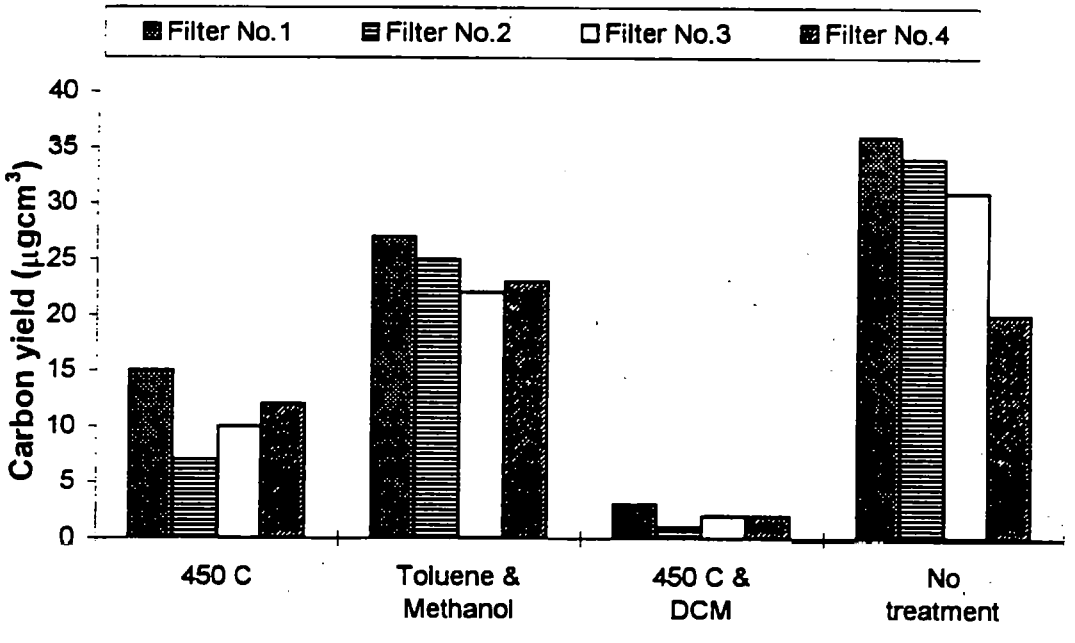

Figure 2.10
A graph to indicate the carbon content of filters with various cleaning treatments.

2.7.1 Carbon isotope analysis

The samples were stored in the dark and to avoid bacterial growth frozen to -15°C until required for analysis. The filters were tested for bacterial growth by placing a piece of stored filter in agar and other nutrient gels to encourage any bacteria to grow. No growth was found to have occurred in any of the filters thus, no bacterial contamination of the samples occurred. The filters were allowed to thaw at room temperature and cut in half. One half was used for trace element analysis, the other was quartered and analysed for carbon content and isotopic composition. The filter quarters were weighed and cut into strips. These strips were transferred into a combustion-cleaned quartz test tube containing excess (approx 0.1 mg) CuO in a quartz bucket at the bottom of the tube. The tube was evacuated, sealed and placed in a muffle furnace for 3hrs at 700°C for combustion to occur. The resulting CO_2 sample was analysed for total carbon yield and isotopic composition with a gas source mass spectrometer.

All sample preparation was performed in clean room laboratories in laminar flow cupboards and all equipment used were cleaned with a 1:1 methanol/toluene mix.

2.7.1.1 Dynamic gas source mass spectrometry

Carbon isotopic analysis was undertaken using a dynamic gas source mass spectrometer, the VG SIRA 24 (Stable Isotope Ratio Analyser). Dynamic gas source mass spectrometers permit the analysis of both sample and reference gas by employing a change-over valve. Gas is allowed to leak through capillaries at a constant rate to a change-over valve, which allows one gas to be admitted into the ion source whilst the other is pumped under high vacuum (Figure 2.11). During this dynamic process both sample and reference gas are depleted at the same rate (initial starting pressures are equalised by adjusting reservoir volumes), and therefore this procedure accounts for differential isotopic fractionation of the samples. A full description of the principles of dynamic gas source mass spectrometry is given in Introduction to Mass Spectrometry (Watson, 1985).

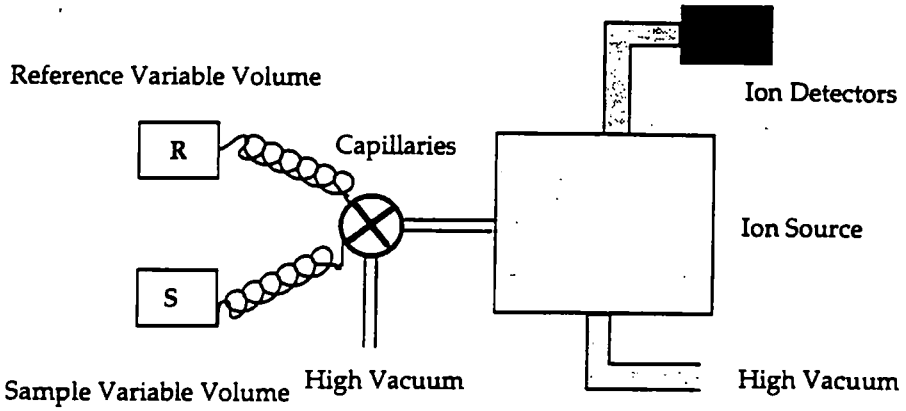

Figure 2.11
A schematic representation of a dynamic gas source mass spectrometer

2.8 Trace element collection and sample preparation

Trace element samples were collected simultaneously with the carbon and Pb samples. From the collected 15 ml 1M HBr, 7 ml was transferred into polypropylene test tube and stored in the dark at room temperature in the clean laboratories in order to prevent photochemical degradation. The HBr was directly used for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis at the NERC laboratory at Royal Holloway College, University of London. The silicate fibre filters were first leached with 5 ml 1M HBr for 2 days, then the filters were removed, the solution centrifuged and decanted off for analysis by ICP-MS.

2.8.1 ICP-MS

In order to perform multi-element (Al, Ba, Co, Cr, Mg, Mn, Ni, Pb, Sb ,V and Zn) analysis on the HBr samples a fast technique was required. ICP-MS was chosen as it has simple preparation techniques and an introduction method with a high sample throughput. ICP

produces sufficient sample dwell time at high temperature in order to produce efficient volatilisation, dissociation and excitation of the sample. A full description of ICP-MS analysis is given in Introduction to Mass Spectrometry (Watson, 1985).

The HBr samples were diluted by a factor of 20 with R.O. H_2O (0.5 ml HBr sample +10 ml R.O. H_2O). The diluted samples were then directly introduced into the plasma as a gas-supported aerosol from a pneumatic nebulizer (Figure 2.12) by blowing a carrier gas, argon, across the mouth of the capillary tube which carries the sample. The nebulizer produces a wide range of droplet size. Droplets of <4 μm diameter (5% of the droplet population) remain supported in the gas and are carried into the plasma. As the aerosol sample approaches the plasma the water evaporates producing solid particles of <0.1 μm diameter. These droplets are rapidly vaporised as they enter the plasma and ionisation occurs (the plasma is typically at temperatures of 7000 to 7500 K). The ions are extracted from the plasma and focused into a beam which is introduced into a quadrupole mass analyser (here the ion beam has a mean energy of 0 to 30 eV). A mass range is then scanned to cover the 12 elements and the data processed.

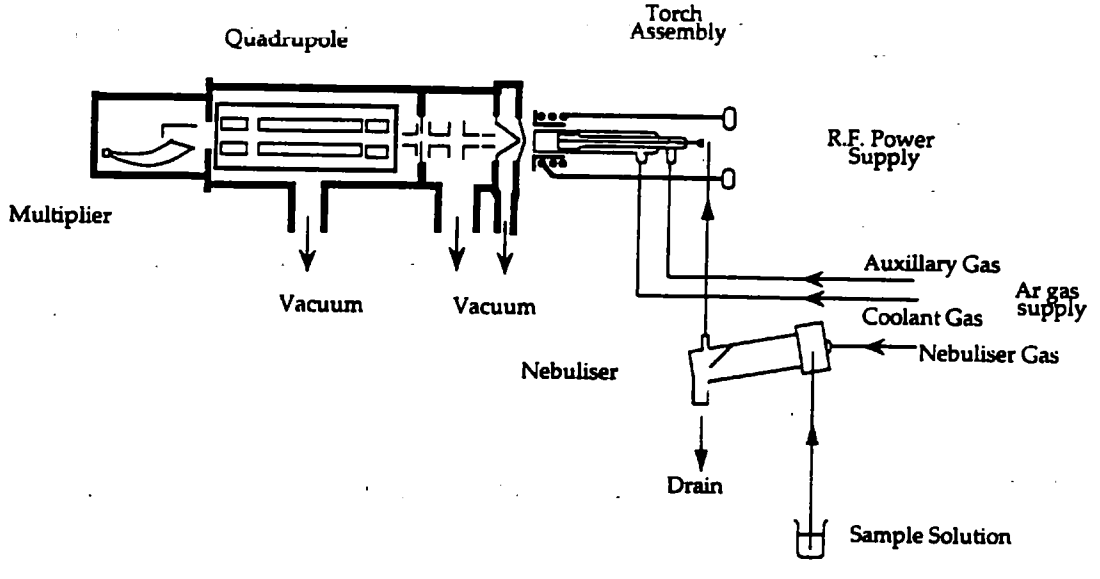

Figure 2.12
A Schematic diagram of ICP-MS with sample introduction by solution nebulisation.

2.8.1.1 Trace Element Standards and Blanks

Stock solutions (10, 20 and 30 ppm) of all elements to be measured were run every 10 samples to monitor and correct for instrument and blank drift ("sample carry-over"). The instrument software then automatically corrected for drift, calculated calibration graphs, and converted ion counts to concentration values.

The detection limits were <0.5 ng ml^{-1} for the elements measured. Each data point represents the mean of 3 individual analyses (blank solution was analysed alternately). Mean percentage accurracy[5] ranged from 79 to 89% (Table 2.0).

Table 2.0

A comparison of the USGS soil standard GXR-2 (Govindarju, 1994) and the measured values indicated that mean percentage accuracy ranged from 79 to 89% for the measured elements.

Element	USGS GXR-2 Soil[6] (ppb)	Measured values (ppb)	Mean percentage accuracy
Al	3118	2650	85
Ba	2240	2231	89
Co	8.6	6.9	80
Cr	36	30	84
Cu	40	32	81
Mg	1410	1199	85
Mn	0.13	0.1	81
Ni	21	18	86
Pb	690	614	89
Sb	49	43	87
V	52	42	80
Zn	530	419	79

Precision was defined as the concordance of a series of measurements of the same quantity. The mean deviation or the relative mean deviation was thus used as a measure of precision. The instrument precision ranged from 0.05 to 1.73% for the elements measured (Table 2.1 and Appendix B(i)).

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[5] *Accuracy was assessed by calculating the percentage difference between the standard and measured values.*

[6] *The soil standard USGS GXR-2 was taken from Park City, Utah, U.S.A.*

Table 2.1

Instument precision was based on trace element relative mean deviation.

Element	Precision (%)
Al	0.39
Ba	0.52
Co	0.40
Cr	0.60
Cu	0.05
Mg	0.23
Mn	0.29
Ni	1.73
Pb	0.83
Sb	0.63
V	0.53
Zn	0.60

HBr, HCl, HNO_3 and clean room blanks were measured (Appendix A(iv) and Appendix a(v)). All the trace element data are quoted as blank corrected (Appendix B(i)). This was achieved by taking the lowest concentration value of each element as the blank.

Chapter 3

The characterisation of aerosols in South Wales and Milton Keynes

3.0 Introduction

Carbon and Pb in the environment have been widely studied (Frey and Corn, 1967a and 1967b; Chow *et al.*, 1969; Dequasie and Grey, 1970; Almqvist, 1974; Patterson and Settle, 1974; Nriagu, 1978; Andreae, 1983; Ashawa *et al.*, 1985; Pacyna *et al.*, 1985; Baeyens *et al.*, 1987; Ball, 1987; Migon and Caccia, 1990; Hamilton and Mansfield, 1991) because of well-documented medical effects on humans, particularly children (Engel *et al.*, 1971; HMSO, 1980; Fachetti *et al.*, 1982, Zielhuis, 1991). Various particle sampling techniques have been used from Hi-volume cascade impactors to Millipore filters. The great majority of this work has focused upon concentration data alone, together with various statistical techniques, such as principal component analysis (PCA) to identify sources of pollutants (Douglas *et al.*, 1985; Alcamo *et al.*, 1992). Recently Sturges and Barrie, 1987[1]; Cachier *et al.*, 1985[2] and Patterson and Settle, 1987[3], began measuring isotopic compositions of Pb and carbon atmospheric particles. In the UK, Sugden (1993), Gibson (1981 and 1984) and Farmer *et al.* (1994) have used Pb concentration and Pb isotopes to identify sources. However, no such work has been attempted in the UK for both C and Pb.

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[1] *At the USA/Canadian border.*

[2] *In central Africa.*

[3] *At a Pacific Island, Enewetork.*

This project has undertaken to clarify the origins of carbon and Pb particles within the atmosphere in Milton Keynes and south Wales using carbon and Pb isotopes as tracers of sources. Tabulated results of carbon and Pb concentrations and isotopic compositions of Milton Keynes and south Wales are reported in this chapter.

3.1 Aims and Objectives

The objectives are:

(1) To achieve a better understanding of Pb and carbon isotopes in aerosols by characterising aerosol sources.

(2) To assess if carbon and Pb isotopes could be used to identify sources of aerosol particles.

(3) To establish if there is a correlation between carbon and Pb isotopic composition and elemental concentration in aerosols.

(4) To identify any relationships between carbon and Pb particles and local weather conditions.

(5) To establish if there were any seasonal variations of the measured elements.

3.2 Sampling strategies

Three sampling strategies were implemented:

(1) South Wales reconnaissance: to ascertain whether Pb and carbon isotopic compositions in aerosol particles varied along 20 sites of the coast and inland, to establish an overview of carbon and Pb variation in the south Wales region and identify main source areas.

(2) Five aerosol source sites in south Wales: in 1991 a reconnaissance field trip was undertaken and Pb isotopic composition was found to vary along the coast, dropping to low ratios at industrial sites (Figure 3.0). However, no distinction could be made between rural and marine samples. In 1992 and 1993 a different field sampling strategy was implemented.

This sampling method was essentially the same (as described in chapter 2) but the sampling locations were selected to establish whether distinct source regions could be characterised. Five sites were chosen to exemplify the regions to be characterised: (a) Swansea - Urban area (b) Port Talbot - Industrial area (c) Rhoscrowther - Marine area with industrial influence (d) Mean Llea - Rural area (e) Broadhaven - Marine area. These source areas were chosen on the basis of the 1991 reconnaissance trip (marine and industrial areas appeared to be the main two sources of Pb) and from the suggested literature sources.

Anthropogenic Pb is predominantly derived from car exhaust (Tatsumoto and Patterson, 1963a & 63b; Chow and Patterson, 1962; Nriagu, 1979). Lead has one of the highest emission rates of any metal, due to its application as an anti-knock agent in petrol and its emission during industrial combustion processes (Nriagu, 1979; Pacyma, 1984). The main natural sources are soil dust (Chow *et al.*, 1973; Shirahata, *et al.*, 1980; Ng and Patterson, 1982; Shen and Boyle, 1987; Hamelin *et al.*, 1990), volcanic activity (Lantzy and Mackenzie, 1979; Nriagu, 1979a; Jaworowski *et al.*, 1981; Gordon *et al.*, 1983; Parcyna, 1982a and Walsh *et al.*, 1979) and marine particles (Tatsumoto and Patterson, 1963a & 63b; Chow and Patterson, 1962; Nriagu, 1979; Walsh *et al.*, 1979; Schaule and Patterson, 1981 & 1982; Jaworowski *et al.*, 1981; Parcyna, 1982a; Gordon *et al.*, 1983 and Hamelin *et al.*, 1989.). Thus, the S. Wales sample sites chosen reflect the main sources: rural (soil source), urban (exhaust sources), industrial and marine.

(3) The Milton Keynes sampling strategy was designed to establish the main sources of carbon and Pb particles within the Milton Keynes atmosphere over a longer time period and assess the relationship between weather conditions and isotopic composition of atmospheric particles. This was achieved by implementing a daily sampling and weather monitoring programme which monitored weather conditions (wet and dry temperature, relative humidity, rain, wind direction and speed). Trace element abundance was also monitored at this site in order to assess if there was an identifiable relationship between the elements monitored and the isotopic values of carbon and Pb.

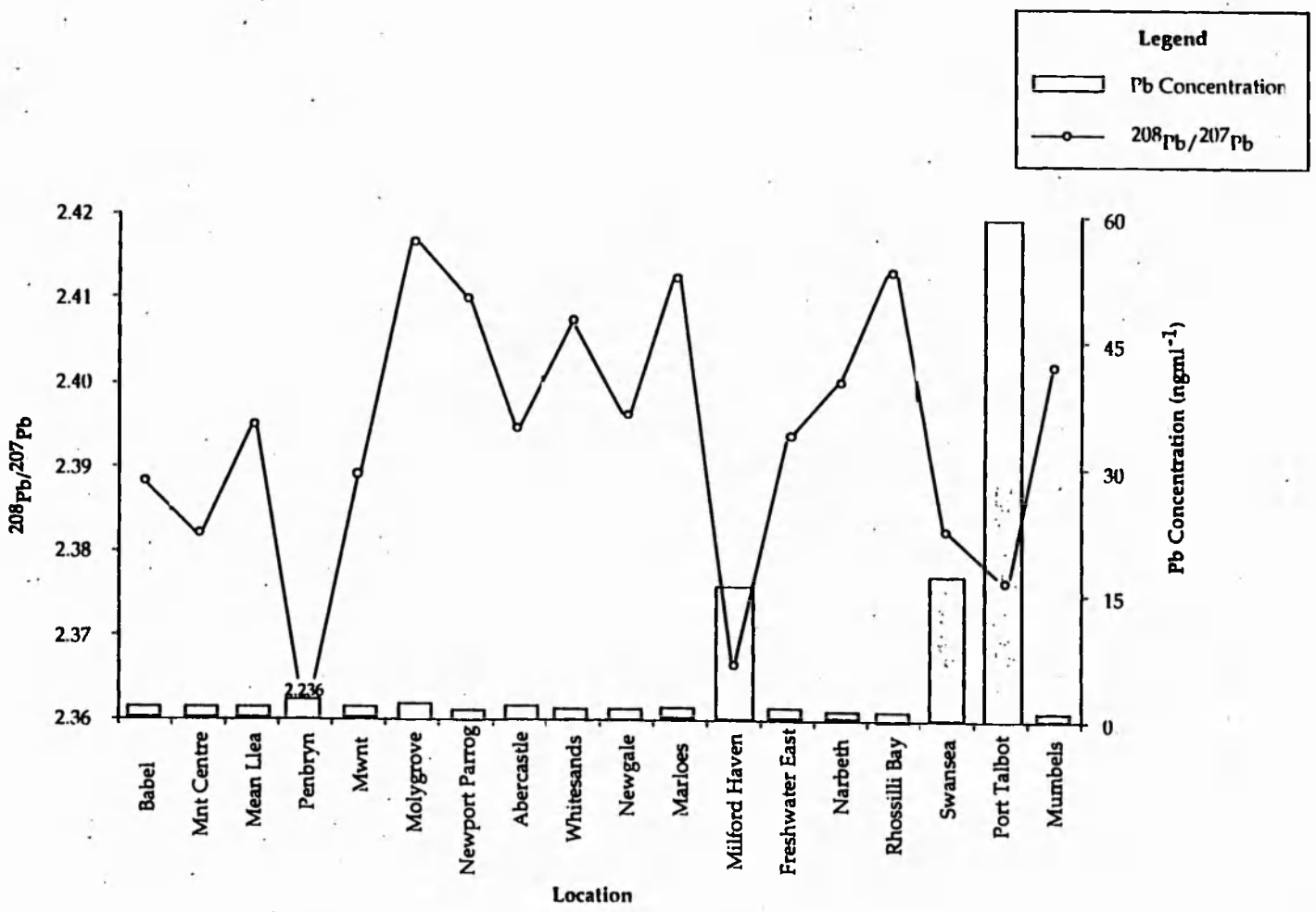

Figure 3.0

The 1991 Welsh aerosol samples indicate that Pb concentration and $^{208}Pb/^{207}Pb$ composition varies along the Welsh coast.

3.3 Carbon and lead identification

There are many sources of atmospheric carbon and Pb, *e.g.* petrol additives, fossil fuel combustion and natural sources such as marine and soil particles. It was beyond the scope and capabilities of this study to investigate such a wide and varied list of sources. Therefore the suspected main sources (seawater, sands, soils, petrol, vehicle exhaust and various vegetation) were analysed for their carbon and Pb isotopic compositions. In this thesis soil is defined as a mixture in varying proportions of organic matter and inorganic particles derived by the weathering of rocks. The inorganic particles of a soil may be derived *in situ* or as a result of transportation. Soil which has been influenced by anthropogenic particles, such as eroded road aggregate, cement, soot and vehicle-derived particles, is regarded as urban regolith. Therefore a two-tier classification is used with rural soil having relatively low anthropogenic input and urban regolith which possess a greater proportion of anthropogenically derived particles.

3.3.1 Vehicles

3.3.1.1 Diesel

Diesel is becoming more important as a vehicle fuel, mainly because of substantial improvements in the performance of diesel engines coupled with increased taxes on leaded fuel. The sale of diesel fuel has doubled from 6.18 million tonnes in 1983 to 11.09 million tonnes in 1992, while leaded petrol sales have decreased from 19.57 million tonnes in 1983 to 12.7 million tonnes in 1992 (Department of Transport, 1994). Another factor in the increased sale of diesel fuel is the increase in the proportion of freight transported by road, which has increased from 53% of total freight transported in 1982 to 61% in 1992 (Department of Transport, 1994).

3.3.1.2 The diesel engine

The diesel engine consists of an assembly of cylinders and pistons attached to a drive shaft and works as follows:

1. The piston descends, drawing air into the cylinder.
2. Ascends, compressing the air to about $\frac{1}{15}$ th of its original volume, raising the temperature to a value that when, towards the end of its stroke, an accurately measured volume of fuel is injected as a fine spray, it ignites immediately.
3. The burning fuel causes the pressure in the cylinder to increase so that the piston is forced down.
4. The cycle is completed by the piston ascending again to drive the burnt gases out of the exhaust pipe (National Society for Clean Air, 1980).

Smoke is produced because the mixing of fuel and air is not sufficiently fast and in the spray there is not sufficient air to achieve complete combustion. Thus, carbon particles form and agglomerate to form soot, which is difficult to burn in the combustion chamber and is emitted as smoke in the exhaust. If a diesel-powered vehicle engine is out of adjustment it produces a smoky exhaust (National Society for Clean Air, 1980).

There are two main problems which arise from smoke emissions. The first is the amenity problem of smoke and the second is the effect on health. Diesel particles have a mass median diameter of 0.02 to 0.1 μg, which allow them to penetrate deeply into the lung (Ball, 1987). In fact, 50% penetrate deep into the pulmonary region. This deep penetration results in two main conditions:

(1) The deposits slow the pulmonary clearance mechanisms (National Research Council, 1981).

(2) The graphitic structure provides numerous adsorption sites for gases and toxic agents (Ball, 1987).

These fine diesel exhaust particles are associated with polyaromatic hydrocarbons (PAHs) (Ball, 1987). Hydrocarbon emissions from diesel engines, for example, PAHs which are proven mutagens and carcinogens, are readily adsorbed onto fine particles. Thus, fine diesel

exhaust particles penetrating deep into the lung may carry toxic substances and this has lead to many medical investigations (National Research Council, 1981; Howe *et al.*, 1983; Schenker *et al*, 1984; Wong *et al.*, 1985).

3.3.1.3 The petrol engine

The conventional petrol engine in motor cars consists of 2 or more cylinder units. For simplicity the operation of one cylinder is discussed. The sequence of events in the operation of a cylinder are summarised thus:

1. A mixture of air and petrol is drawn in as the piston descends.

2. The inlet valve closes and the piston ascends to the top of its stroke (compressing the charge by 8 to 9 times).

3. The charge is ignited by an electric spark from the sparking plug and the heat released by the combustion of the petrol increases the pressure and the piston is driven down by the expanding gases.

4. This energy turns the crankshaft. The exhaust valve opens and as the piston returns to the top of its stroke the combustion gases are driven out into the exhaust manifold.

3.3.1.4 Petrol additives

Until recently, engine designers were aiming to increase efficiency by aiming at higher combustion temperatures achievable by the use of high compression ratios. These conditions produce combustion which tends to become explosive and 'knocking' occurs, which harms the engine. Knocking or premature combustion, can be reduced by the addition of tetra-alkyl lead to the petrol.

The degree to which petrol resists knock is defined by reference to an artificial scale of octane numbers. The scale is derived from the knock resistance of a mixture in varying proportions of two pure hydrocarbons; n-heptane (low knock resistance) and iso-octane (high knock resistance). The percentage of iso-octane in the mixture is the octane number. For example, 97 octane petrol will start to knock in the test engine at the same point as a mixture of 3% n-heptane and 97% iso-octane.

There are two main tests to determine octane number:

1. Research Octane Number (RON) simulates acceleration from low speeds (conditions in which audible knock occurs).

2. Motor Octane Number (MON) simulates driving at high and constant speed.

The difference between RON and MON is called the sensitivity of fuel to temperature. The marketing of petrol states the RON of petrol, the British standard specification for 4 star (premium) petrol is a minimum of 97 RON/86MON.

The most widely used Pb additives used to achieve high RON and MON are tetra methyl and tetra ethyl lead. These alkyl lead compounds are partially combusted in the engine, producing organic Pb compounds which are responsible for the majority of Pb species in the atmosphere (Broekaert *et al*, 1989). The primary Pb-containing particles that are emitted into the atmosphere are approximately 0.1 μm in diameter. The particles rapidly coagulate with other carbonaceous material and form structures of up to 1 μm mean diameter. In the UK, Octel is the only company that produces the alkyl Pb used by all petrol manufacturers and so it could be expected that all Pb in petrol would have the same isotopic composition. In order to ascertain whether the Pb isotope ratio varied in petrol additives and thus altered the Pb isotopic composition of the exhaust emission particles, petrol Pb isotopic compositions were monitored for 4 months (September and December, 1992; January and February, 1993). The Pb isotopic values of 2 brands of petrol (Esso and BP) in Milton Keynes and Swansea were analysed (Appendix B(ii)).

Recent concerns over air pollution in Europe, has resulted in the restriction of the Pb content in petrol, for example in 1985 to 0.15 g l^{-1} (European Economic Community, 1985). Unleaded petrol production has been achieved by high octane petrol with no Pb. Unleaded petrol currently accounts for more than 50% of the UK fuel market (Department of Transport, 1994).

3.3.1.5 Exhaust

The exhaust fumes exhibit a mean $^{208}Pb/^{207}Pb$ of 2.33 (stdev = ± 0.11) and concentration of 0.12 ng ml^{-1} (± 0.018) to 10.7 ng ml^{-1} (± 0.016). The concentrations of Pb in petrol vary

from 76.9 to 4.3 ng ml^{-1}, this is in agreement with Octel data for Pb which also varies from 10 to 100 ng ml^{-1} (Octel, 1993). O'Connor *et al.*, (1990) working in Perth, Western Australia, also noted that the concentration of Pb additive varied substantially from 0.39 gl^{-1} to 0.80 gl^{-1} for premium grade petrol in just one month in 1986. The exhaust samples have a broad range of $^{207}Pb/^{204}Pb$ ratios. The samples have lower $^{208}Pb/^{207}Pb$ ratios and higher $^{204}Pb/^{207}Pb$ ratios than petrol (Appendix B(ii) and Figure 3.1). The particle exhaust samples indicate that Pb particles emerging from exhaust emissions have a different isotopic ratio from the original tetra methyl/ethyl Pb additive. The cause of this variation is not known, but it could be an aggregate of values caused by variations of Pb derived from many sources of Pb in alkyl Pb used during the lifetime of the sampled months. Octel obtains its Pb ores from Trail in Canada and Mount Isa and Broken Hill in Australia (Associated Octel personal communication, 1993). Table 3.0 indicates the Pb isotopic values of these ores and tetra methyl/ethyl lead additive and vehicle exhaust.

Table 3.0

Average petrol and Pb ore isotopic values.

Sample	$^{208}Pb/^{207}Pb$	$^{204}Pb/^{207}Pb$	Reference
Mount Isa, Australia	2.323	0.06441	Chow, 1970
Broken Hill, Australia	2.322	0.06453	Chow, 1970
Average petrol	2.326	0.06473	
Min	2.326	0.06436	Cutajar, *et al.*, 1995
Max	2.334	0.06499	

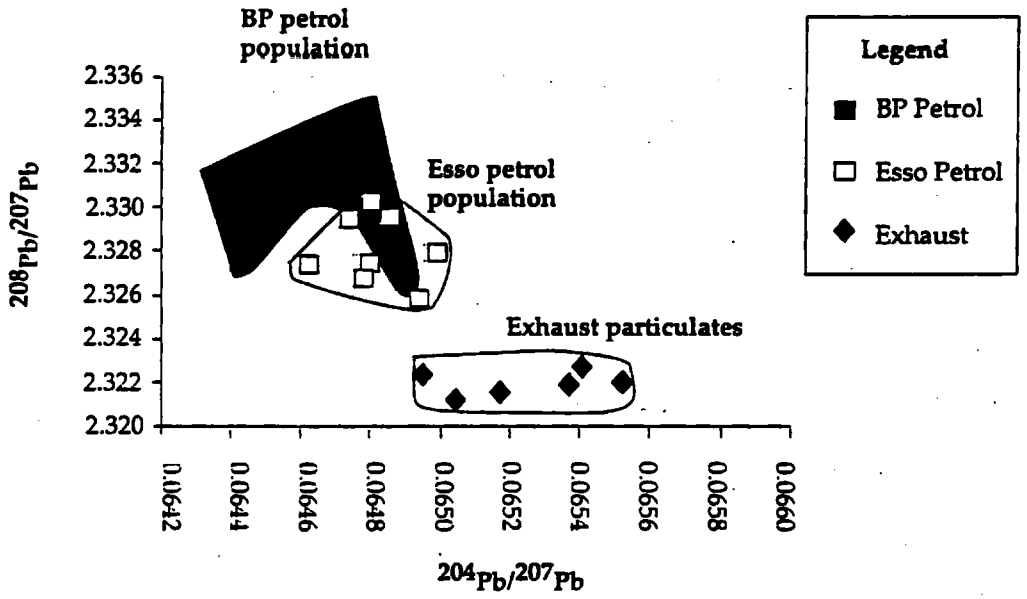

Figure 3.01.
The $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ ratios of Esso, BP Welsh petrol and Exhaust particulates. Three distinct regions are identified; (1) BP petrol, (2) Esso petrol and (3) Exhaust particulates.

3.3.2 Sediments and Soils

The Pb isotope ratios of soils and sands depend greatly upon the source rock from which they are formed. Milton Keynes is underlain by Oxford Clay and the south Wales sample sites are underlain by a complex suite of igneous and sedimentary rocks. Thus it would be expected that the Milton Keynes and south Wales soil would have different isotopic compositions. The top few cm of the soil column is affected by pollutant particles that have settled out from the atmosphere such as exhaust emission particles. Such pollutants affect the top layer of soil and their contribution to the soil is of greater importance when considering soils in close proximity to roads (<20 m). This is because most Pb particles are deposited within 20 m from their origin (Smith, 1976). Thus, urban soils (Swansea and Milton Keynes) are affected by vehicle emissions because of the greater density of roads (Daines, *et al.*, 1970) compared to a rural area, such as Mean Llea. Since the top soil is considered to be of importance in the supply of particles to the atmosphere, only the top 5 cm of soil was sampled in this study.

In order to measure Pb isotopic values of soils/sediments, samples were taken from various sites. Approximately 10 g of the top 5 cm of the soil/sediment were sampled and dried at 100°C for 2 days. The samples were then sieved to produce a homogenous powder. Approximately 0.1 g of soil/sediment was dissolved in a pre-cleaned Teflon bomb by the addition of HNO_3 and 48% HF as descibed in chapter 2 section 2.5. Half of the residue was removed and leached with 1 ml 1 M HBr to remove the Pb within the soil/sediment. The leached and untreated samples underwent the same Pb concentration procedure as the aerosol samples (Table 3.1 and Figure 3.2). No difference was found between the isotopic compositions of the leached and untreated samples (Table 3.1). The Broadhaven sample concentrations are a factor of two lower than the other sample sites. This may be due to the Broadhaven samples being predominantley sand grains.

Table 3.1

Soil and sand sample results for Milton Keynes, Rhoscrother and Mean Llea soils, Swansea and Broadhaven sands.

+Sand samples were not leached. *n.a. = no data available.

Sample	$^{208}Pb/^{207}Pb$	$^{204}Pb/^{207}Pb$	Pb Concentration ($\mu g\ g^{-1}$)
Milton Keynes	2.465 (± 0.0001)	0.0641 (± 0.0001)	0.01 (± 0.0001)
Leached	2.464 (± 0.0002)	0.0642(± 0.0001)	n.a. *
Mean Llea	2.449 (± 0.0001)	0.0643(± 0.0001)	0.01 (± 0.0001)
Leached	2.450 (± 0.0005)	0.0643 (± 0.0001)	n.a.
Rhoscrowther	2.469 (± 0.0002)	0.0649 (± 0.0001)	0.02 (± 0.0001)
Leached	2.468 (± 0.0002)	0.0641(± 0.0001)	n.a.
Broadhaven	2.439 (± 0.0001)	0.0646 (± 0.0001)	0.06 (± 0.0001)
Leached	2.439 (± 0.0006)	0.0646 (± 0.0001)	n.a.
Broadhaven (sand)+	2.393 (± 0.0010)	0.0644 (± 0.0001)	0.002 (± 0.0001)

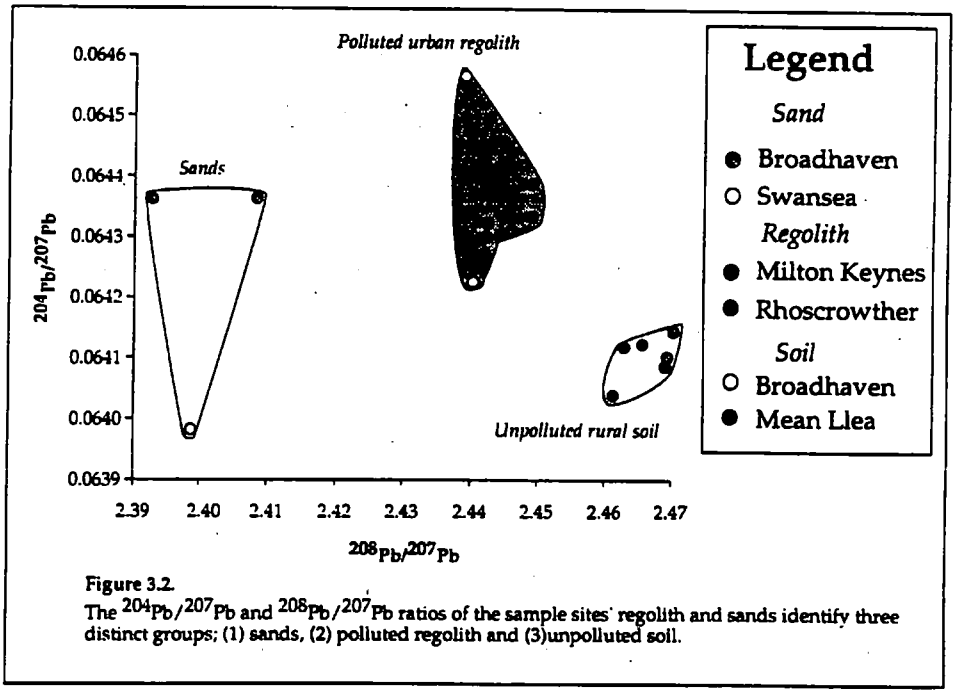

Figure 3.2.
The $^{204}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the sample sites' regolith and sands identify three distinct groups; (1) sands, (2) polluted regolith and (3)unpolluted soil.

The $\delta^{13}C$ values of soil are much more complex than Pb isotopic compositions and will depend upon many factors such as soil fauna and flora, the percentage and type of organic matter, time of year, soil bulk, *etc.* The bulk combustion of soils would be of no use, since all organic material would be combusted. The resulting $\delta^{13}C$ values would be meaningless, since the organic composition of the soil contains a varied mix of fauna and flora, which would vary both temporally and spatially. Thus no $\delta^{13}C$ values are given for soils or sands.

3.3.3 Geology

The geology of the site is important in contributing to Pb particles within the atmosphere. Weathering products contribute to soil composition and macroscopic particles such as sand grains, which may eventually become aerosol particles. The importance of the geology as a source of Pb particles will depend heavily upon the vegetative cover of the site, because of the binding effect of vegetation.

Weather also plays an important role in the availability of surface materials for atmospheric particles. Wet and dry particles are of different mass and so require different wind speeds in order to be picked up and incorporated into the atmosphere. Therefore, wet conditions increase the weight of particles, and consequently the wind speed necessary for wet particles to be transported into the atmosphere is increased. Thus, a freshly ploughed and dry field will be a greater source of Pb particles than a field in crop.

The Welsh sample site geology is varied and too complex to describe for the purposes of this thesis. A summary is provided in Table 3.2.

3.3.3.1 Milton Keynes geology

Glacial erosion and deposition have modified the soils of the area (Horton *et al.*, 1974). In general terms, the area can be best considered as a dissected boulder clay plateau, with the rivers Ouse and Ouzel cutting across Oxford Clay with Blisworth and Cornbrash limestones forming strong features to the north. Pleistocene and Recent deposits conceal the solid rock formations over half of the Milton Keynes area. Boulder clay outcrops throughout the area. This boulder clay is an erosional remnant of an ice sheet which once blanketed the

entire district. The sample site is on a 3-storey-high flat-roofed building at Walton Hall which stands upon boulder clay. The clay consists of unsorted sediments deposited during glacial epochs (Horton *et al.*, 1974). Freyer (1942) states that approximately 75% of the soil in the Milton Keynes area can be described as a clayey soil due to the combination of boulder clay and the clay formations in the area.

The Pb isotopic compositions of the Welsh and Milton Keynes soils/sediments are tabulated in Table 3.1. These results indicate that each of the soils/sediments vary in isotopic composition indicating different sources. It is interesting to note that mean Milton Keynes and Rhoscrowther $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ isotopic compositions have similar values and can be grouped together (Figure 3.2). These soils have quite a different Pb isotopic composition from the mean Mean Llea and Broadhaven soil $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ isotopic compositions. The urban soils which are in close proximity to roads have been found to be influenced by petrol. Milton Keynes and Rhoscrowther soils have been classified as the polluted urban soils/regolith with Mean Llea and Broadhaven soils the unpolluted rural soils. Mean Swansea $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ isotopic values are different to mean Broadhaven values. This is indicative of industrial pollution in Swansea which mixes with aerosols derived from Broadhaven sand to produce the polluted Swansea value.

Lead in sands has been found to be less concentrated than in soils. Sands are mainly composed of silica with trace elements, such as Pb and iron derived from erosion. Soils, however obtain their Pb from local source rock and pedological processes, such as biodegradation. Another interesting point is that the soil samples can be divided into 2 groups: polluted urban and unpolluted rural soil (Figure 3.2 and Table 3.1).

Table 3.2.

A brief tabulated geological description of the Welsh sites based upon the Institute of Geological Science Maps 52N06W, 51N04W, 51N06W and 52N04W.

Site	Geology	$^{208}Pb/^{207}Pb$ [4]	$^{204}Pb/^{207}Pb$	Age
Mwnt, Penbryn, Parrog and Molygrove	Calcareous Flags and Goodwick shales.	2.42 - 2.47	0.0641 - 0.0642	Ordovician
Abercastle	Lingula Flags (Grey silty shales and thin grit beds).	2.39- 2.42	0.0642 - 0.0643	Upper Cambrian
Newgale	Solva bed and Caerbwdy sandstone (purple and green sandstone with mudstones).	2.39- 2.42	0.0642 - 0.0643	Cambrian
Whitesands	1. Pebidian volcanic series (acid and intermediate tuffs, volcanic conglomerates and grits). 2. Brunel beds (sandstones and sandy mudstones). 3. Solva bed and Caerbwdy sandstone (purple and green sandstone with mudstones).	>2.39 2.42 - 2.47 2.39- 2.42	>0.643 0.0641 - 0.0642 0.0642 - 0.0643	PreCambrian Lower Ordovician Cambrian
Freshwater East	Carboniferous limestone and Limestone shale.	2.42 - 2.47	0.0641- 0.0642	Lower. Carboniferous
Rhossilli Bay	Old red sandstone (Sandstone shales).	2.42 - 2.47	0.0641- 0.0642	Carboniferous
Mumbles	Limestone	2.42 - 2.47	0.0641- 0.0642	Carboniferous
Milford Haven	Red Marl Group (red siltstones and mudstones and sandstones).	2.42 - 2.47	0.0641- 0.0642	Devonian
Port Talbot and Swansea	Lower Coal measures	2.42 - 2.47	0.0641- 0.0642	Carboniferous
Narbeth	Murchison and Bifidus shales (grey and black shales).	2.42 - 2.47	0.0641 - 0.0642	Ordivician
Mean Llea, Mountain centre and Seam Helen	1. St. Maughans and Raglen formations (sandstones and mudstones). 2. Clee formation and Brownstones group (Sandstones, conglomerate and siltstones).	2.42 - 2.47	0.0641 - .0642	Silurian Lower Devonian
Marloes	Gray sandstone group (sandstones and siltstones)	2.42 - 2.47	0.0641 - 0.0642	Devonian
Rhoscrowther	Milford Haven Group (Red and brown siltstones with subordinate sandstones, local basal conglomerate).	2.42 - 2.47	0.0641 - 0.0642	Devonian
Broadhaven	Limestone	2.42 - 2.47	0.0641- 0.0642	Lower. Carboniferous

[4] *George, et al., (1970) stated that the geological age of the rocks in this area is mainly Upper and Mid Palaeozoic (225 to 500Myrs). Thus, this age range was used to determine Pb isotopic values using a 2-stage Pb evolution model (Stacey and Kramers, 1975).*

3.3.4. Seawater

The present ionic composition of seawater results from a balance between the rate at which dissolved matter is added to the ocean from the land and the atmosphere, and the rate at which it is removed from the sea by incorporation into the soils/sediments or by being returned to the atmosphere. The main dissolved Pb species are Pb^{2+}, $PbOH^{+}$ and $PbCl^{+}$ (Riley and Chester, 1971). Materials enter the ocean either by fall-out from the atmosphere or the influx of river water. Since the concentration of the various elements in seawater approximate to a steady state, the rates at which they are supplied to the ocean are balanced by the rates at which they are removed. Barth (1952) introduced the concept of the residence time of an element (T) which is the average time it remains in the sea before being removed. Thus,

$$T = \frac{A}{dA/dt}$$

where,

A= Total amount of the element dissolved or in suspension in the ocean.

$\frac{dA}{dt}$ = Rate an element is added or precipitated.

Using this method Pb has been found to have an oceanic residence time of 2×10^{3} yrs (Goldberg, 1965). Residence time has been found to reflect the mixing time of an element (x 3-4 residence time). When Pb residence time is compared with Na (2.6×10^{8}) and Mg (4.5×10^{7}) it becomes apparent that Pb has in fact a relatively short residence time. This reflects the efficiency with which Pb is removed from solution (Chester and Riley, 1971). Thus, the concept of residence time implies that anthropogenically derived Pb, of which the initial output occurred some 150 years ago, would not have fully integrated into the ocean. High concentrations would be expected to occur along the continental shelf, where anthropogenic Pb is derived.

Seawater samples were taken from Broadhaven (remote marine site) and Swansea (urban site). The Broadhaven seawater $^{208}Pb/^{207}Pb$ values range from 2.381 to 2.408 and the $^{204}Pb/^{207}Pb$ values 0.0636 to 0.0640, with Swansea $^{208}Pb/^{207}Pb$ values ranging from 2.393 to 2.409 and $^{204}Pb/^{207}Pb$ values from 0.0639 to 0.0641 (Figure 3.3). The Swansea and Broadhaven values cluster together into a group, indicating that the Pb at these sites may have a common source, sea spray.

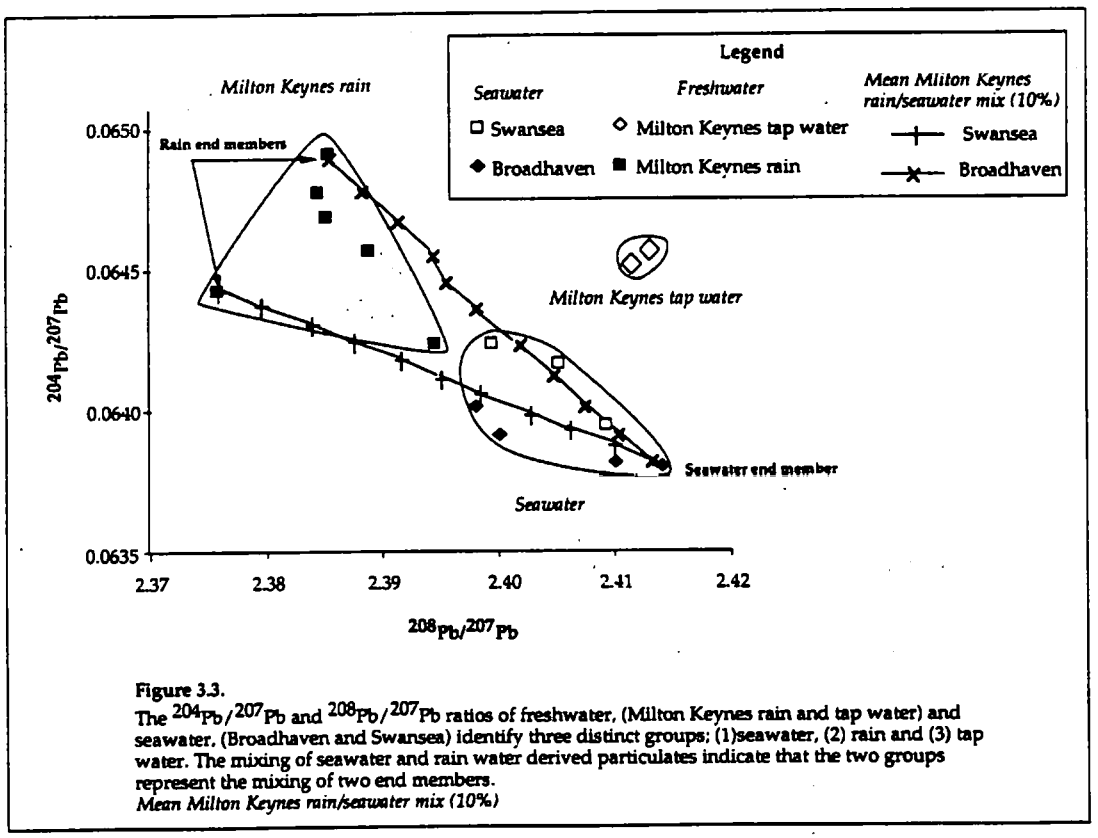

Figure 3.3.
The $^{204}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of freshwater, (Milton Keynes rain and tap water) and seawater, (Broadhaven and Swansea) identify three distinct groups; (1)seawater, (2) rain and (3) tap water. The mixing of seawater and rain water derived particulates indicate that the two groups represent the mixing of two end members.
Mean Milton Keynes rain/seawater mix (10%)

3.3.5 Identified sources

Four separate Pb aerosol source groups have been characterised (Figure 3.4). These source groups are seawater, petrol, sands and soil (Table 3.3).

These Pb sources will be used throughout this thesis and be depicted in figures as max.-min. fields.

Table 3.3

The mean $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ isotopic compositions of seawater, petrol, exhaust, sand and soils are tabulated. These isotopic compositions characterise 4 main aerosol source groups with 6 individual sources of Pb particles and rain. Rain is a mechanism of deposition and is represented as Milton Keynes Wet deposition.

Source	$^{208}Pb/^{207}Pb$ (mean)	$^{204}Pb/^{207}Pb$ (mean)
Source 1		
Seawater	2.367	0.0639
Source 2		
Petrol		
Milton Keynes	2.330	0.0647
Welsh petrol	2.332	0.0651
Exhaust	2.326	0.0654
Milton Keynes Wet deposition	2.385	0.0648
Source 3		
Sand	2.400	0.0642
Source 4		
Soils		
Urban polluted regolith (Rhoscrowther and Milton Keynes)	2.443	0.0644
Rural unpolluted soil	2.466	0.0641

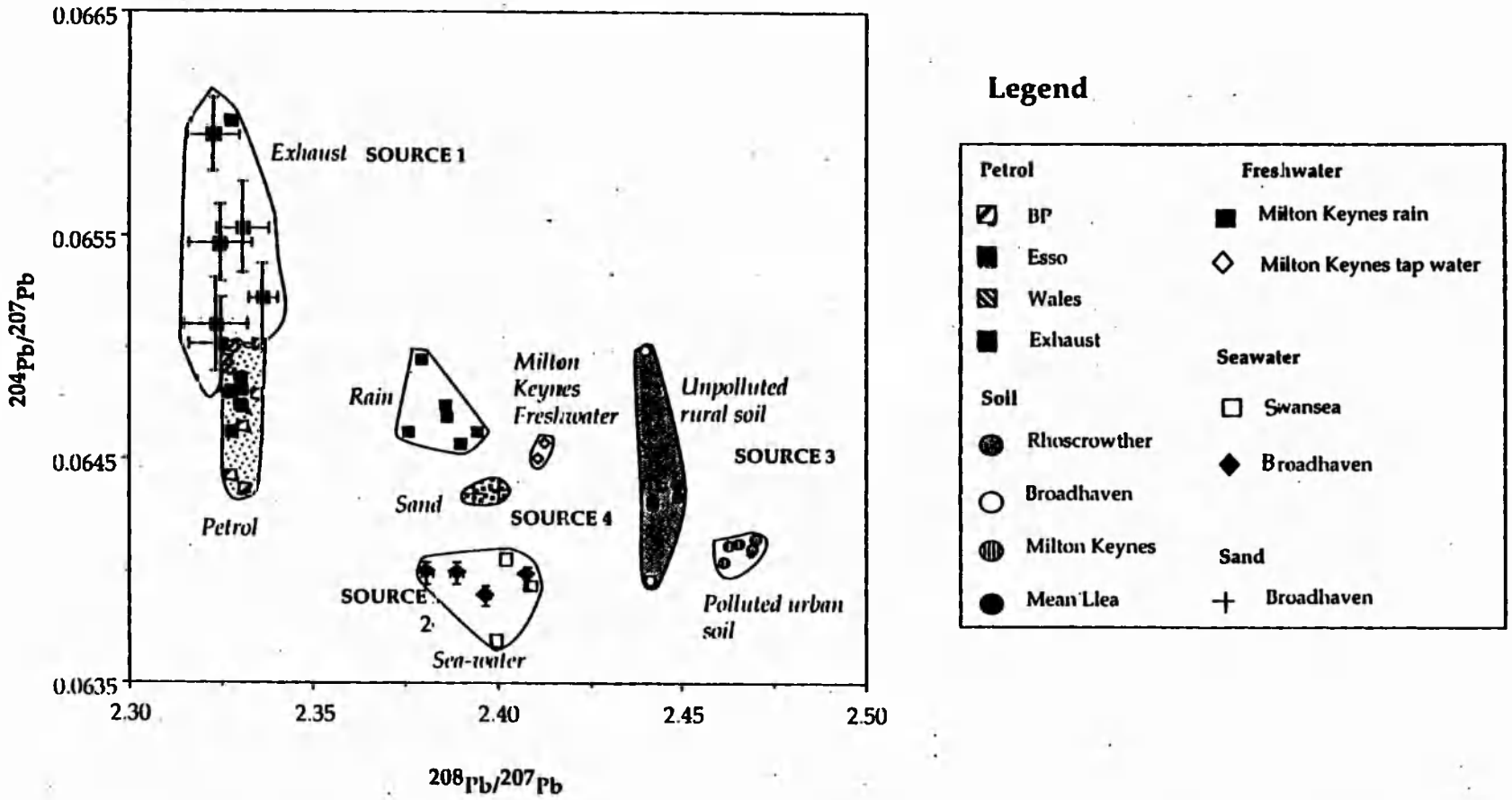

Figure 3.4.
The $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ ratios of all measured sources of Pb produce 8 distinct groups; (1)polluted soils, (2)unpolluted soils, (3)Broadhaven sand, (4)Milton Keynes tap water (5)Milton Keynes rain, (6) seawater, (7)petrol and (8) exhaust.

3.4 Milton Keynes results

3.4.1 Concentration and isotope ratio results

3.4.1.1 Carbon

The carbon concentration and isotopic composition for the Milton Keynes site exhibited a temporal variation (Jan. 1992 to April 1993) from mean C concentrations of 7.94 (± 0.11) to 64.04 μg cm^{-3} (± 0.3), $\delta^{13}C$ values of -9.52 (± 0.14) to -28.36 ‰ (± 0.03) (Figure 3.5). $\delta^{13}C$ values are comparable to data from Brémond *et al.*[5] (1989) but C concentrations measured by Heintzenberg and Winkler[6] (1984) are not (urban concentrations of 10 to 80 ng m^{-3}). This discrepancy may be explained by the varied sources of C in the urban environment. Figure 3.6 indicates that the C concentrations exhibited a weak positive correlation with time ($r = 0.435$, $p<0.0001$), Figure 3.6 and Appendix B(iii)).

It was possible to establish a periodic temporal fluctuation in carbon parameters (Figures 3.5 and 3.6).

(1) January to October 1992.

The samples in this period are generally low in carbon concentrations and vary from 10 to 41 μg cm^{-3} (mean = 23 μg cm^{-3}). The $\delta^{13}C$ values vary from -27 to -10 ‰ (mean = -18 ‰). In order to clarify any temporal variation within the dataset running averages[7] were calculated and are plotted in Figure 3.5. The carbon concentration running averages were found to vary from 8 to 64 μg cm^{-3} (mean = 25 μg cm^{-3}) with variations of $\delta^{13}C$ values from -10 to -28 ‰.(mean = -18 ‰).

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[5] *Brémond et al. (1989) $\delta^{13}C$ values in Paris, France 1986-1987.*

[6] *Heintzenberg and Winkler (1984) carbon concentrations of 10 to 80 ngm^{-3} in Hamburg, Germany.*

[7] *Running averages were calculated by averaging every 3days data.*

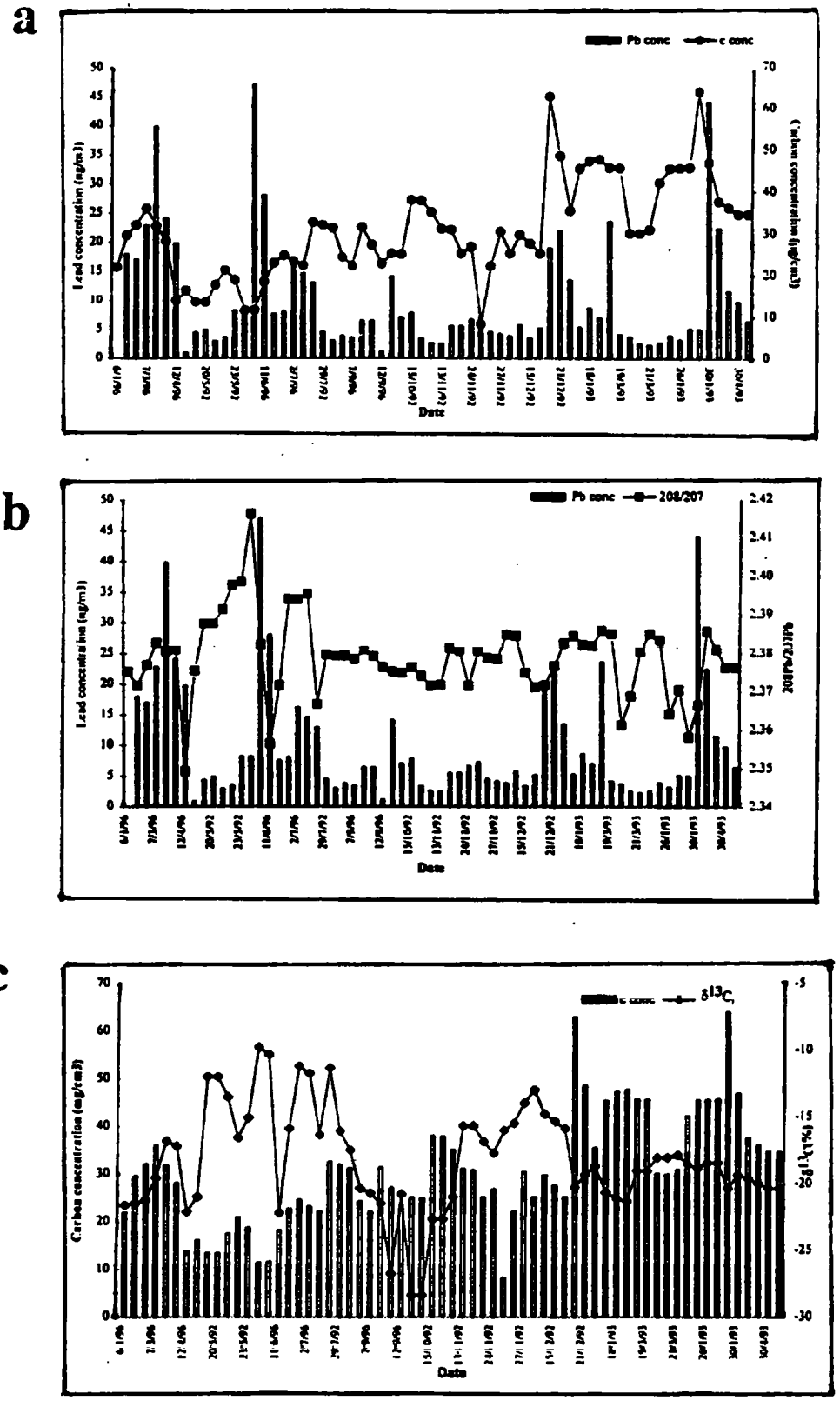

Figure 3.5

The running averages of Milton Keynes data; (a) The running averages of Milton Keynes Pb and C concentration data identifies a variation with time (b) The running averages of Milton Keynes $^{208}Pb/^{207}Pb$ and Pb concentration (c) $\delta^{13}C$ values and C concentration data identifies a variation with time.

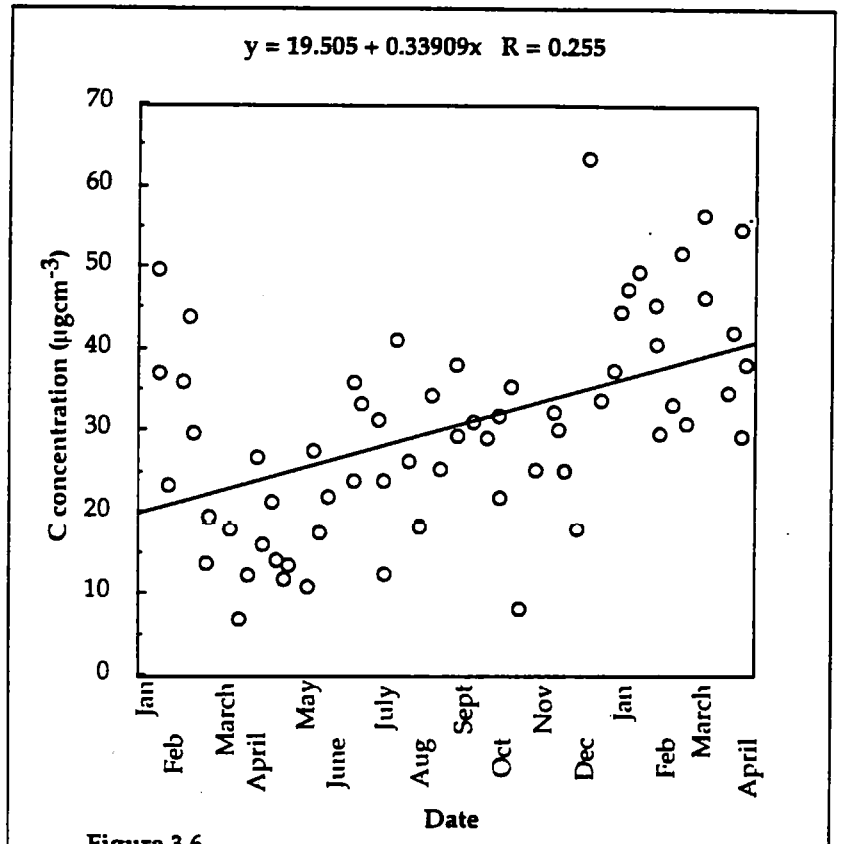

Figure 3.6
Temporal variations in carbon concentration at the Milton Keynes site.

(2) November 1992 to April 1993

The samples in this period are generally high in carbon concentration (Figure 3.5) and vary from 8 to 64 µg cm^{-3} (mean = 37 µg cm^{-3}). The $\delta^{13}C$ values are relatively stable from -21 to -13 ‰ (mean = -18 ‰).

3.4.1.2 Lead

The Pb concentration and isotopic composition for the Milton Keynes site also varied with time from 1 ng m^{-3} (± 0.02) to 56.70 ng m^{-3} (± 0.2) $^{204}Pb/^{207}Pb$ ratios from 0.0649 (±0.0001) to 0.0685 (±0.001) and $^{208}Pb/^{207}Pb$ ratios from 2.348 (±0.0001) to 2.416 (±0.0001) (Appendix A (ii)). The Pb concentrations are comparable to those found by

Migon *et al.*[8] (1993) and Nichelson and Branson[9] (1993). From these data it was possible to identify a periodic change in Pb parameters. Running averages[10] of concentration and isotopic composition were used in order to smooth out the sharp and marked irregularities, so that only the major fluctuations are stressed in order to simplify assessment of the data. Running averages of concentration and isotopic composition were found to exhibit temporal fluctuations (Figure 3.5).

(1) January to September 1992.

The samples in this period are generally constant in $^{204}Pb/^{207}Pb$ ratios (0.0635 to 0.0666). $^{208}Pb/^{207}Pb$ ratios exhibit relatively large variation ($^{208}Pb/^{207}Pb$ = 2.349 to 2.416). These values exhibit greater $^{208}Pb/^{207}Pb$ ratios than the October-April samples. The Pb concentrations are generally high and vary from 1 to 47 ng m^{-3} (mean = 12 ng m^{-3}).

The January to September 1992 samples are generally low in carbon concentration but the Pb concentrations are generally high. $\delta^{13}C$ values vary widely, whereas with stable $^{204}Pb/^{207}Pb$ ratios and relatively large variations in $^{208}Pb/^{207}Pb$ ratios. The Pb concentration period (January to November 1992) appears to lag behind the isotope ratios which indicates that concentration response time to temporal variation may be affected by more complex processes which have a longer response time than the isotopic compositions and carbon concentrations.

(2) October 1992 to April 1993.

The samples in this period generally exhibit a an increased variation in $^{204}Pb/^{207}Pb$ ratios (0.0612 to 0.0666). However, the $^{208}Pb/^{207}Pb$ ratios are relatively stable (2.358 to 2.386). These values exhibit lower $^{208}Pb/^{207}Pb$ ratios than the January-September samples. The Pb concentrations are lower and vary from 2 to 44 ng m^{-3} (mean 9 ng m^{-3})

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[8] *Migon* et al. *(1993) work in N.W. Mediterranean, 1986 to 1992, concentrations of Pb 10 ngm^{-3}*

[9] *Nichelson and Branson (1993) work in Manchester and Brent, UK., 1988 to 1991, 100+ ngm^{-3}*

[10] *The running average was taken as the average of 3 weeks that is, the first average is the average of 1 to 3 weeks; the second average is 2 to 4 etc.*

These samples are generally high in carbon concentrations, but the Pb concentrations are low. $\delta^{13}C$ values and $^{208}Pb/^{207}Pb$ ratios are stable, with a large variation of $^{204}Pb/^{207}Pb$ ratios. The Pb concentration period (December 1992 to April 1993) again lags behind the isotope ratios which indicates that concentration response time to temporal variation may be affected by more complex processes which have a longer response time than isotopic compositions and carbon concentrations.

t-test

The running average helps to identify temporal variations. In order to assess the reliability of these temporal fluctuations a t-test was performed on the dataset to assess the difference between the sampling years data. The unpaired 2 group t-test compares two normal sample means determined from two independent samples. Statistically, it is assumed that the two means have been defined by samples from the same population and therefore the difference between the means are to be 0;

$$H_o: p_1 = p_2$$

$$H_1: p_1 \neq p_2$$

Where,

H_o = Hypothesis

H_1 = Alternative hypothesis.

Thus, the statistical analysis addresses the question of whether or not the observed difference between the two means is a chance difference or not. The analysis was calculated using StatView (4.01). The two populations assessed were those identified by carbon and Pb concentration and isotopic fluctuations, Jan. to Oct. 1992 and Nov. 1992 to April 1993. The results are listed in Appendix B (iv). The temporal characteristics identified by the t-test are briefly discussed below.

The t-test indicates that a statistically significant difference exists between Jan. to Sept. 1992 and Oct. 1992 to April 1993 for $^{204}Pb/^{207}Pb$ ratios ($\alpha = 0.05$ and $t = -1.16$) and $\delta^{13}C$ values ($\alpha = 0.05$ and $t = -1.80$). Therefore, a temporal variation for the dataset was established. However, Pb concentration and $^{208}Pb/^{207}Pb$ composition did not exhibit a

significant difference (Appendix B (iv)). These results indicates the incomplete nature of the dataset. However, for the purpose of this discussion it is assumed that only $^{204}Pb/^{207}Pb$ ratios and $\delta^{13}C$ values are associated with temporal fluctuations.

3.4.1.3 Annual fluctuations

The variation in the dataset may indicate a mix of particles derived from diesel and petrol emissions producing variations in isotopic compositions in 1992, which decrease with decreasing petrol emission influence in 1993 (Table 3.5). The t-test results may indicate that the differences between 1992 and 1993 $^{204}Pb/^{207}Pb$ ratios and $\delta^{13}C$ values represent the decrease in the number of vehicles using leaded petrol.

Table 3.5

Department of transport statistics indicate that the numbers of diesel and unleaded petrol driven vehicles has increased from 1982 to 1992 (Department of transport, 1994).

*In millions of tonnes.

*Fuel	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
Leaded petrol	19.57	20.23	20.4	21.47	22.18	22.99	19.27	16.05	14.15	12.7
Unleaded petrol	-	-	-	-	-	0.26	4.63	8.26	9.87	11.2
DERV	6.18	6.75	7.11	7.87	8.47	9.37	10.12	10.65	10.69	11.09

The increased use of unleaded petrol can also be identified by carbon and Pb concentrations. In 1992 high Pb and low carbon concentrations were observed. This probably indicates that there has been a decreased use of leaded petrol, with increased carbon output from all vehicles. This may be an indication of the decreasing influence of leaded petrol vehicle emissions and the increase in diesel vehicles or DERV emissions (Table 3.5) in the UK. This phenomenon has also been observed in the Welsh samples for the same time period. Pattenden and Branson (1987) and Nicholson and Branson (1993) have also observed temporal fluctuations of Pb concentration. These authors noted that Pb levels in urban air

increased in some winter months, which was attributed to the presence of a temperature inversion that restricted pollutant dispersal.

3.4.1.4 Carbon and lead relationships

When carbon and Pb parameters are considered together there is an apparent relationship between carbon and Pb. The $^{208}Pb/^{207}Pb$ ratios and $\delta^{13}C$ values for the Milton Keynes site exhibit a weak positive correlation ($r = 0.431$, $p < 0.0001$). In fact low $^{208}Pb/^{207}Pb$ ratios are associated with high concentrations of heavy carbon values. This possible relationship indicates that $^{208}Pb/^{207}Pb$ ratios are related to light $\delta^{13}C$ values. The $\delta^{13}C$ values and $^{208}Pb/^{207}Pb$ ratios also indicate 2 main wind direction related groups (Figure 3.7):

(a) West-Southwest; This group ranges from a $^{208}Pb/^{207}Pb$ ratio of 2.36 to 2.39 and $\delta^{13}C$ values of - 13 to - 23 ‰, which is thought to indicate a vehicle component.

(b) North-West; This group ranges from a $^{208}Pb/^{207}Pb$ ratio of 2.38 to 2.40 and $\delta^{13}C$ values of -17 to -9 ‰, which is thought to indicate an urban regolith component.

The carbon concentration and $^{208}Pb/^{207}Pb$ ratios were found to be negatively related with a correlation coefficient of 0.43. Carbon and Pb isotopic compositions and concentration were found to indicate two distinct sources, which agree with the wind direction-dependent groupings (Figure 3.7):

(a) This group exhibits low $^{208}Pb/^{207}Pb$ ratios with light $\delta^{13}C$ values and relatively high carbon concentrations ($\delta^{13}C$ values of -23.1 ‰ (± 0.1) to -14.8 ‰ (± 0.1), $^{208}Pb/^{207}Pb$ ratios of 2.367 (± 0.0001) to 2.376 (± 0.0001) and carbon concentrations of 18.35 to 63.08 $\mu g\ cm^{-3}$).

(b) This group exhibits high $^{208}Pb/^{207}Pb$ ratios with heavy $\delta^{13}C$ values and relatively low carbon concentrations ($\delta^{13}C$ values of (± 0.04), -9.5 ‰ to -18.4 ‰ (± 0.04), $^{208}Pb/^{207}Pb$ ratios of 2.394 (± 0.0003) to 2.416 (± 0.0003), and carbon concentrations of 8.29 to 32.29 $\mu g\ cm^{-3}$).

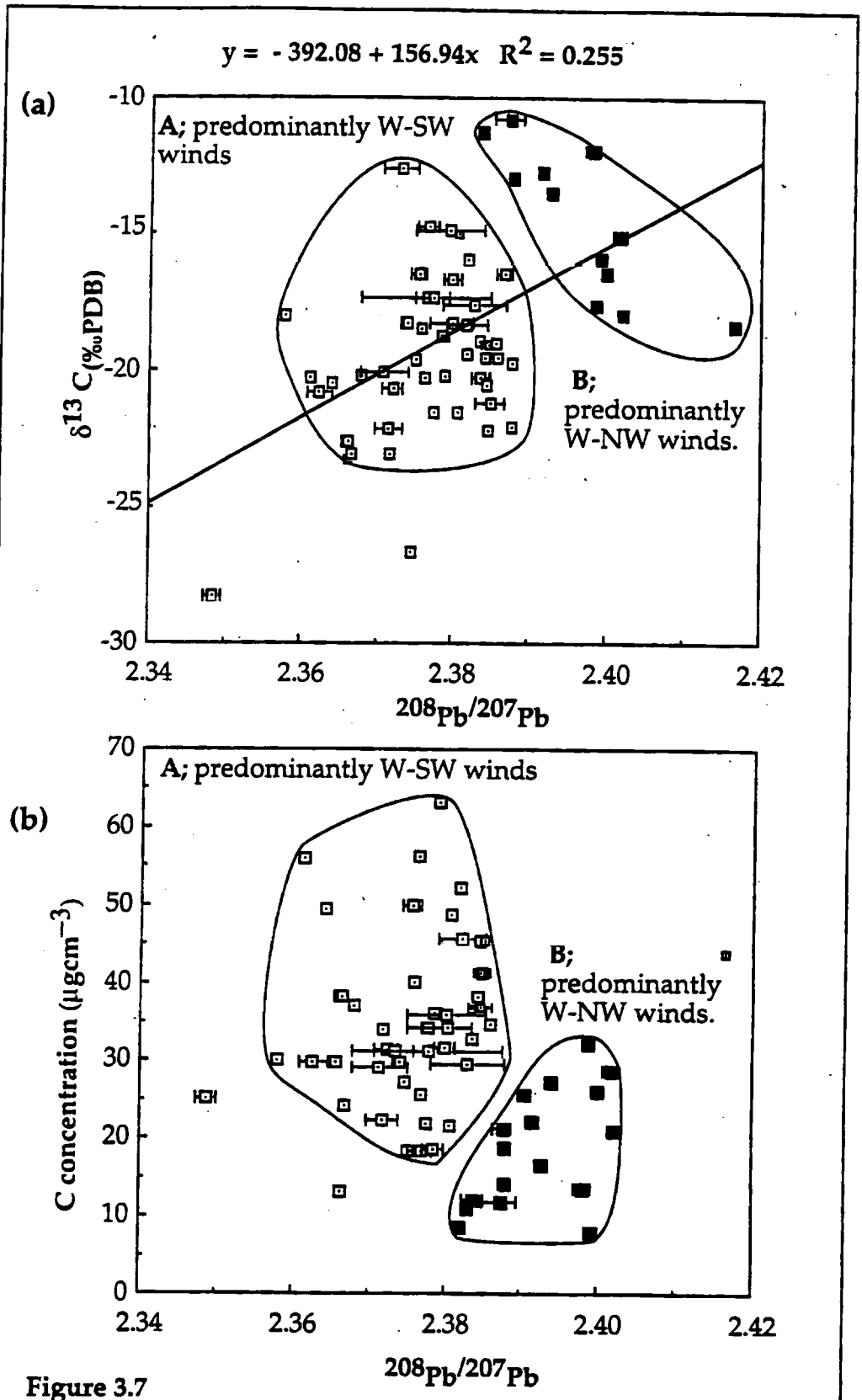

Figure 3.7
Pb and C isotopic composition data of the Milton Keynes site. (a) Two discrete groups which are wind direction dependant; A (dominantly W-SW) and B (dominantly W-NW), (b) C concentration and $^{208}Pb/^{207}Pb$ composition data divide into two discrete groups which are wind direction dependent; A (dominantly W-SW) and B (dominantly W-NW).

3.4.2 Statistical Analysis

The correlation coefficients of the data indicated that there was a weak relationship between the carbon and Pb variables, with a t-test indicating that a temporal fluctuation was also present. Therefore, in order to clarify the relationship between carbon, Pb and ambient variables such as rain and wind direction, a factor analysis was performed on the Milton Keynes dataset.

3.4.2.1 Factor Analysis

The initial factor extraction method was by principal components, with no transformations, using the StatView (4.01) program. This factor extraction method determines the magnitudes of communality estimates of the variables. These in turn influence the magnitudes of the eigen-values, which ultimately influence decisions regarding the number of factors to extract. Principal component analysis is the oldest and most widely used factorising procedure. It performs a single eigenvalue-eigenvector analysis of the correlation matrix in the original form.

In factor analysis, the association within a set of m variables is considered as reflecting the correlations of each variable with p mutually uncorrelated factors (Davis, 1973). It is assumed that p<m. Therefore, variance in the m variables is determined from variance in the p factors, the common factors. In addition, a contribution is made by singular sources which exclusively affect the m original variables, the unique factor (Davies, 1973). The factor model can be expressed simply as:

$$X_j = \sum_{r=1}^{p} l_{jr} f_r + \varepsilon_j$$

where,

f_r = r^{th} common factor.

p = specified number of factors.

ε_j = random variation, unique to the original variable X_j (there are m random variables, ε_j).

l_{jr} = the loading of the j^{th} variate on the r^{th} factor.

The results of the factor analysis are tabulated in Table 3.4.

Table 3.4

Factor analysis results of Milton Keynes data identify 3 factors with 60 degrees of freedom. The level of factor loading significance was taken as >0.5 and are represented in bold type.

Variable	Factor 1 (38% variance)	Factor 2 (31% variance)	Factor 3 (30.4% variance)
$^{204}Pb/^{207}Pb$	0.237	**0.610**	0.358
$^{208}Pb/^{207}Pb$	**0.647**	0.394	-0.254
Pb concentration	0.104	0.001	**0.612**
$\delta^{13}C$	**0.799**	0.277	-0.134
carbon concentration	**-0.631**	0.423	0.075
Rain	-0.416	0.001	**-0.552**
Wind direction	-0.109	**0.591**	**0.548**

Three main factors were identified:

Factor 1

This factor shows high loadings for the $\delta^{13}C$ values, $^{208}Pb/^{207}Pb$ ratios and negative loading for carbon concentration variables, accounting for 38% of the variance in the Milton Keynes samples. This component relates carbon concentration and isotopic composition and is independent of Pb concentration, rain and wind direction. This is thought to indicate a soil/regolith component, which would be expected to remain relatively constant. For clarity this will be discussed as the soil component.

Factor 2

This factor shows high positive loadings for $^{204}Pb/^{207}Pb$ ratios and wind direction variables. This indicates that the $^{204}Pb/^{207}Pb$ ratios are heavily influenced by wind direction. For the Milton Keynes site this factor accounts for 31.1% variance in the data. The association of $^{204}Pb/^{207}Pb$ ratios and wind direction are thought to be related to periodic change. For example, October 1992 to April 1993 samples are characterised by relatively large variations of $^{204}Pb/^{207}Pb$ ratios and south-westerly wind directions, while the January to

September 1992 samples are characterised by slight variations of $^{204}Pb/^{207}Pb$ ratios and Northerly wind directions. This factor may represent a vehicle component and not a biomass affect. This is because biomass sources would be expected to be independent of wind direction.

Factor 3

This factor shows high positive loadings for Pb concentration and wind direction with negative loadings for the rain variables. This factor accounts for 30.4% of the variance in the Milton Keynes samples. It is suggested that this factor supports the supposition that Pb particles are washed out of the atmosphere by rain. This factor is thought to represent a vehicle component which would be expected to be both wind direction- and rain-dependent (see below).

Therefore, factors 1 and 3 together account for 68.8% of the sample variation and are representative of the influence of rain on both concentration and isotopic composition. This relationship identifies rain as a major influencing component in the generation and/or transportation/depositional mechanisms of carbon concentration (which increase with rain) and Pb concentration (which decreases with rain) within the atmosphere. Periodicity was also identified in the dataset by factor 2 which represents the influence of wind direction on $^{204}Pb/^{207}Pb$ composition. It is suggested that periodic effects are of primary importance with daily weather conditions, such as wind direction and rain, being the dominant factors, within individual samples.

The factor components were used to identify end members of mixing model calculations. Therefore, in order to establish if the mixing of urban regolith (Factor 1) and petrol emission (Factors 2 and 3) derived particles could produce Milton Keynes aerosol values a mixing model with the two identified factor analysis components, urban soil ($^{208}Pb/^{207}Pb$ 2.463 and $^{204}Pb/^{207}Pb$ 0.0641) and vehicle derived particles ($^{208}Pb/^{207}Pb$ 2.326 and $^{204}Pb/^{207}Pb$ 0.0654), were used as end members. Although there is a wide spread of data in figure 3.8, this model produced a mixing line which accounts for the majority of the Milton Keynes data (Model 1, Figure 3.8). All mixing model calculations for both Milton Keynes and Wales data are tabulated in Appendix B(V).

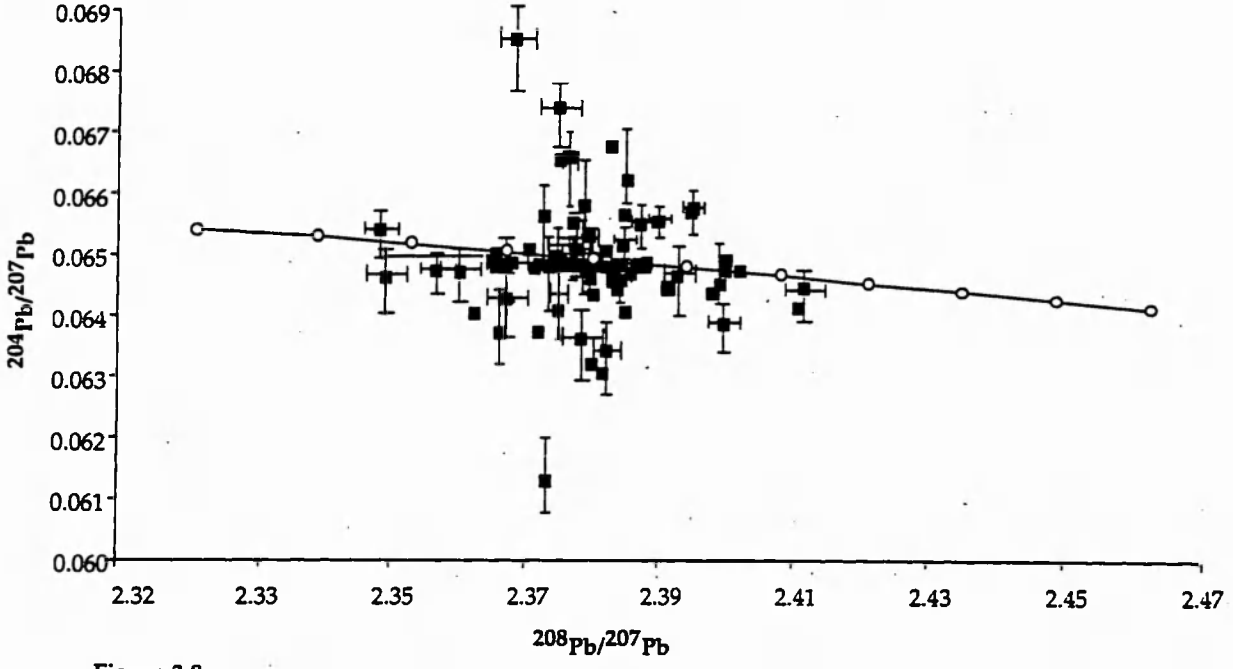

Figure 3.8
Model 1 (Appendix B(iii)); A mix of Milton Keynes regolith-derived aerosol and exhaust-derived aerosol, (○). The majority of the Milton Keynes data, (■) can be seen to lie within the mixing model end members.

3.4.3 Weather

The temporal characteristics can be related to weather. The weather parameters monitored were: wind speed and direction, wet and dry bulb temperatures, relative humidity and rain.

Rain

January to October 1992 samples that are low in Pb concentrations, were taken on days when there had been no rain for at least 2 days and November 1992 to April 1993 samples were taken during rain or shortly after rain. This relationship with rain is reflected in Pb concentration and $^{208}Pb/^{207}Pb$ ratios (Figure 3.9).

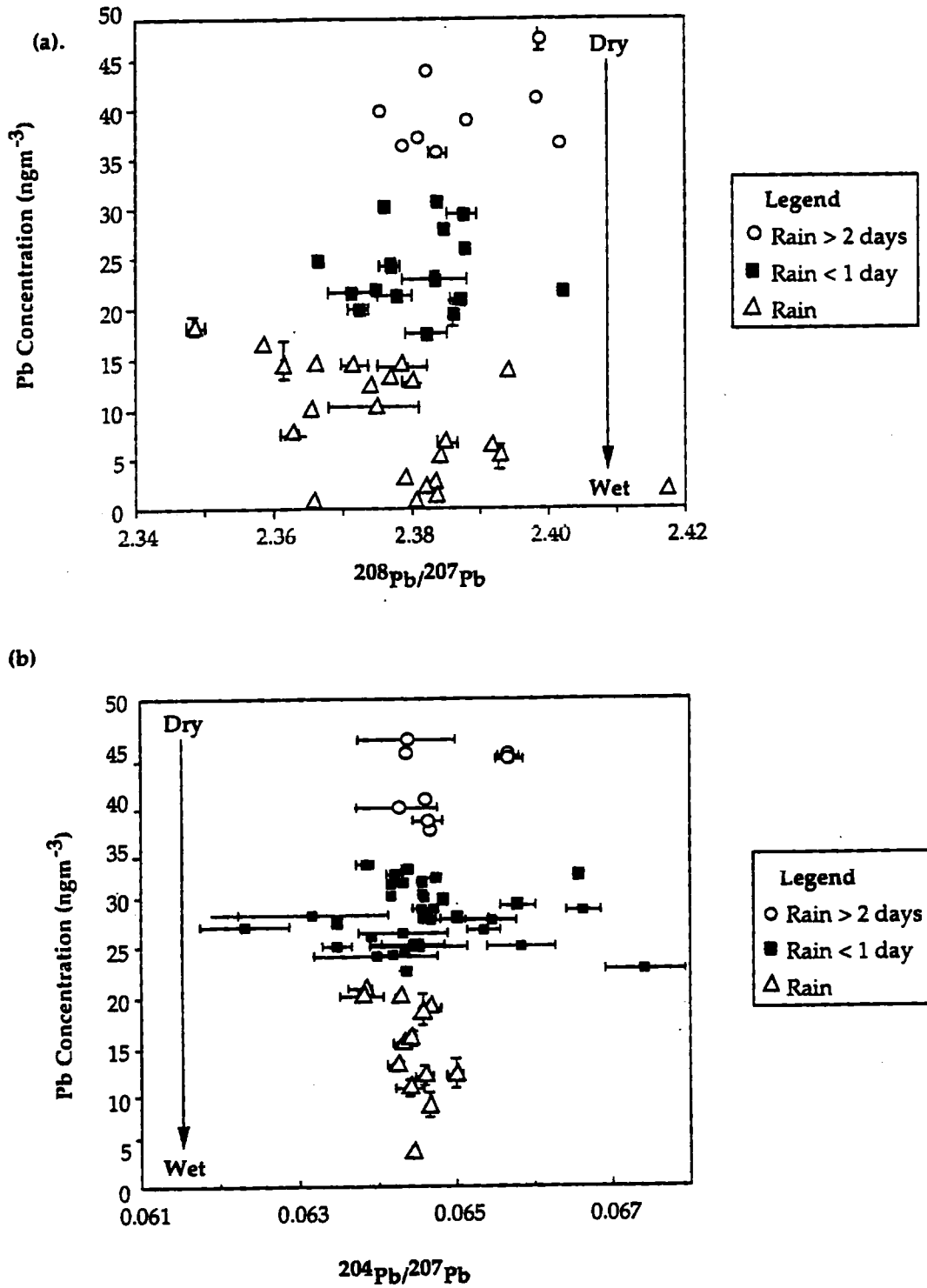

Figure 3.9
Pb concentration and isotopic composition data indicate a relationship with rain; (a). $^{204}Pb/^{207}Pb$ compositions are influenced by wet and dry weather conditions. Samples taken during wet periods exibit a realtively lower Pb concentration than those taken during dry conditions. An isotopic shift to lower 'petrol-like' values are associated with a decrease in Pb concentration during wet weather conditions, (b) Pb concentration and $^{208}Pb/^{207}Pb$ compositions are influenced by wet and dry weather conditions. Samples taken during wet periodsexibit a realtively lower Pb concentration than those taken during dry conditions. An isotopic shift to lower 'petrol-like' values are associated with a decrease in Pb concentration during wet weather conditions.

It was also identified by factor analysis, which indicated an association between carbon concentration, $^{208}Pb/^{207}Pb$, $\delta^{13}C$ values and rain (Factor 1), and Pb concentration, wind direction and rain (Factor 3). Lead particles are may be 'washed-out' of the atmosphere during a rain episode, resulting in a decrease in atmospheric particle concentrations. The period that encompasses the greatest number of rain episodes (October 1992 to April 1993) exhibits low Pb concentrations. However, it must be noted that this interpretation is based upon a limited dataset. Migon *et al.* (1993) also noted that increased rainfall in the north-west Mediterranean was associated with a decrease in Pb concentration, and they also found that Pb concentration varied with season; Autumn 1987, which contained three rain events of >60 mm of rain, was associated with low Pb concentrations, $<20\mu g\ l^{-1}$. Hicks and Shannon (1979) and Ashawa *et al.* (1985) found that rain intensity was also important in Pb concentration in rain water: short rain episodes produced greater Pb concentrations in rain water than longer episodes, indicating that Pb particles are rapidly washed out of the atmosphere. Carbon particles have also been found to be washed-out by rain but with no clear relationship exhibited.

During rain the Pb isotopic composition does not remain static (Figure 3.9): it is reduced ($^{208}Pb/^{207}Pb$ ratio Dry_{mean} = 2.389 (± 0.01) and Wet_{mean} = 2.379 (± 0.009)). It is tentatively suggested that this observation can be explained by vehicle emission sources increasing in importance during rain; that is, the continuous output of Pb from vehicle exhaust emissons exerts an immediate and continuous influence on the aerosol. When rain 'washes out' Pb particles from the atmosphere, the vehicle derived particles are immediately re-introduced into the atmosphere. This produces a *juvenile*[11] Pb isotopic signature, with a shift towards the petrol $^{208}Pb/^{207}Pb$ isotopic composition of 2.33 and thus the wet $^{208}Pb/^{207}Pb_{mean}$ of 2.379 is achieved. This juvenile aerosol is short-lived and is only present before mixing of other Milton Keynes sources can take place. After rain the aerosol will mature and particles from other sources will be incorporated to produce the dry

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[11] *Juvenile Pb isotopic signature is defined as the primary isotope signature associated with background Pb sources (natural).*

$^{208}Pb/^{207}Pb_{mean}$ of 2.389, which partly masks the Pb vehicle component. Thus, this tentative explanation of the data requires further work and it is suggested that a sampling regime be undertaken specifically to investigate this hypothesis further.

It is expected that other rain conditions will further affect carbon and Pb particles within the atmosphere. For example, precipitation type (snow/rain) (Hicks and Shannon, 1979; Ashawa *et al.*, 1985) and atmospheric pressure would affect transportation, deposition and generation of aerosols.

Wind direction

In the discussion only local sources are considered; however it is expected that long distance transportation is important within this fine particle size. Nevertheless, it was felt that no reasonable limits could be placed on such a discussion, and therefore only local sources are discussed.

The hypothesis that carbon and Pb are influenced by fluctuations in the use of leaded petrol can be tested by examining the dominant wind direction for the 1992 and 1993 sample days. For the time period January-September 1992 the wind direction was dominated by north-westerlies. The main Pb and carbon source to the north of the sample site is the busy M1 motorway. The M1 is approximately 4 km north of the sample site and the vehicles which use it are a large source of carbon and Pb in the atmosphere. A northerly wind would transport vehicle derived particles to the sample site[12] resulting in air masses that are high in Pb. Such an association of Pb concentration and isotopic composition with wind direction agrees with work by other authors (Sturges and Barrie, 1987, 1989a and 1989b; Patterson and Settle, 1974).

October 1992-April 1993 samples where dominated by south-westerly winds. This wind direction would have been influenced by both agricultural land and local industry. To the south of the sample site lies Bletchley, further south lies agricultural land. Particulates

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[12]*The majority of Pb particulates are deposited 20m from source. However at the 0.5μm size range, (the size that is considered in this study) the particulates remain suspended in the atmosphere, where they can be transported to greater distances.*

influenced by this area would be high in carbon concentration (agricultural/industrial areas) but relatively few Pb sources. The only anthropogenic source of Pb in this direction is the A5 trunk road. Both the A5 and the M1 are heavily influenced by temporal and spatial variables:

(i) Time, peak road use by vehicles is 8 to 9am and 5 to 6pm.

(ii) Weather, rain increases the use of vehicles for travel to work.

(iii) Holidays, during public holidays there is an increase in traffic (Department of Transport, 1990).

At an atmospheric front, the wind speed and direction changes (Barry and Chorley, 1978) and a relationship between wind speed and direction and rain was expected. However, no such relationship was identified. This is thought to reflect the lack of sufficient short timescale data.

Lead and carbon isotopic compositions can also support the hypothesis that there are two distinct, wind direction-dependent sources of carbon and Pb. The January-October 1992 samples which exhibit low Pb concentrations are dominantly subject to north-westerly winds. The January-October 1992 samples have characteristically petrol-influenced Pb and carbon isotopic compositions. The $^{208}Pb/^{207}Pb$ ratios range from 2.34 to 2.37 and $\delta^{13}C$ values of -28 to -17.5 ‰ which are strongly influenced by vehicle emissions (petrol exhibits $^{208}Pb/^{207}Pb$ ratios of 2.33 and $\delta^{13}C$ values of -25 to -30 ‰). However, the October 1992-April 1993 samples that are characterised by relatively low Pb concentrations and high carbon concentrations, with dominantly west-south-westerly wind directions, exhibit Pb and carbon isotopic compositions influenced by local urban regolith. The $^{208}Pb/^{207}Pb$ ratios range from 2.38 to 2.42 and $\delta^{13}C$ values of -9 ‰ to -22.5 ‰ (urban regolith $^{208}Pb/^{207}Pb$ = 2.462). However, it must be emphasised that it is expected that there is substantial mixing between petrol emissions, urban regolith and other minor unidentified sources.

The model illustrated in Figure 3.8 indicates that a mixing of soil and vehicle emissions derived particulates account for some of the Milton Keynes aerosol samples. Therefore, wind direction and speed may affect the isotopic composition of the aerosol samples and may account for the spread of values in Figures 3.8 and 3.10.

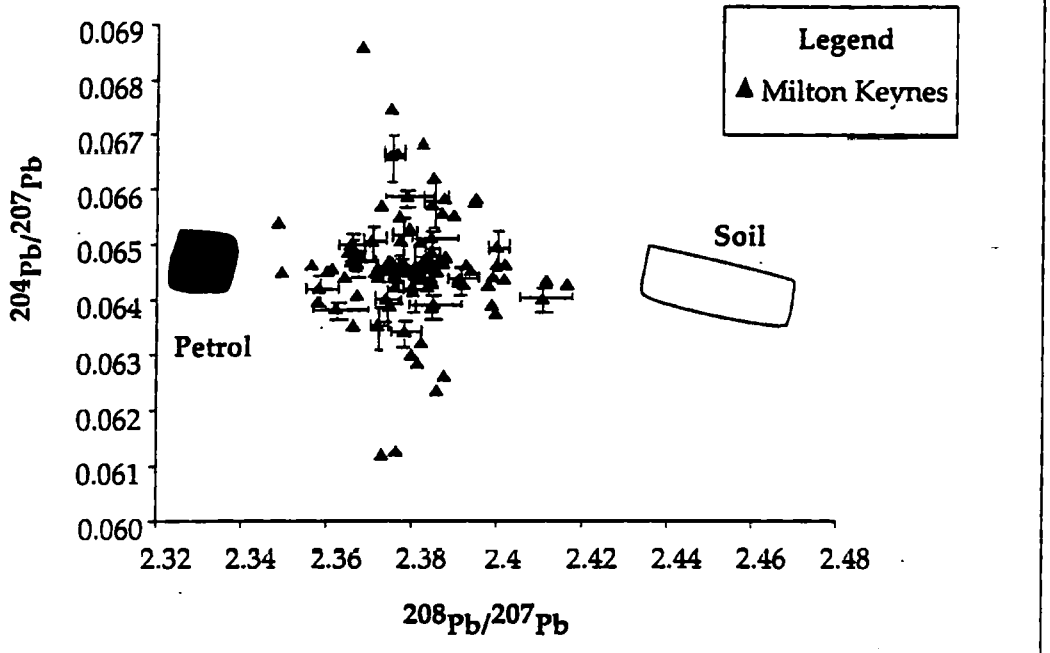

Figure 3.10
The Pb isotopic ratio data of the Milton Keynes site lie between the soil and petrol fields.

Temperature and humidity

The main weather parameters that influence the carbon and Pb particles within the atmosphere are rain, humidity and wind direction. A minor parameter not yet discussed is temperature. Temperature correlates poorly with $^{208}Pb/^{207}Pb$ ratios ($r = 0.21$, $p<0.05$) but exhibits a moderate negative correlation with carbon concentration ($r = -0.53$, $p<0.0001$). Such a relationship may relate to rain and wind direction, which have already been found to influence carbon and Pb.

Humidity did not significantly correlate with Pb and carbon variables. However, occult deposition (mist and dew) would be expected to be important.

3.4.4.1 Daily variations

In each of the months May, November 1992 to January 1993 daily samples were taken for a period of a week. This daily sampling procedure was carried out in order to establish daily carbon and Pb variations. Each month is discussed separately.

18th to 24th May, 1992

All the carbon and Pb parameters varied throughout the week; For example, on the 21/5/92 an increase in Pb concentration from 7.85 ng m^{-3} to 47.0 ng m^{-3} was identified (Figure 3.11). This increase in Pb concentration is attributed to the burning of material to the East of the sample site. So, as the burning material liberated Pb particles into the atmosphere, the south-westerly wind transported these particles to the sample site. However, carbon concentration does not mirror the increase in Pb concentration. This indicates that the conditions of burning were such as to produce relatively large carbon particles (>0.5 μm) which were not sampled (Figure 3.11). The $\delta^{13}C$ values are thought to represent fractionation of a light source to heavy values or the mixing of two sources. Therefore, the 19th to 22nd of May represent days when biological fractionation or stratospheric fractionation occured (-22 to -12 ‰) during transportation. The 24/5/92 represents an input of new carbon into the aerosol, with isotopically heavy carbon. The carbon sources for this week are thus not constant and indicate mixing which represents a isotopically dynamic situation.

The $^{208}Pb/^{207}Pb$ ratios could also be explained by the mixing of two other sources, local urban regolith particles ($^{208}Pb/^{207}Pb$ = 2.462) and vehicle emissions derived Pb ($^{208}Pb/^{207}Pb$ = 2.33). These two other sources are wind speed-dependent, with the regolith signature dominating on days with relatively high wind speeds of 2.1 to 3.4 ms^{-1} when urban regolith particles are incorporated into the aerosol (Figure 3.11). Conversely, on the 21/5/92 the $^{208}Pb/^{207}Pb$ signature decreased from a mean of 2.388 to 2.396. This is related to low wind speeds (0.6 to 1.1 ms^{-1}) reducing the regolith input and producing a more vehicle-related signature. When petrol emission $^{208}Pb/^{207}Pb$ ratios ($^{208}Pb/^{207}Pb$ = 2.327 and 2.335) are mixed with Milton Keynes regolith ($^{208}Pb/^{207}Pb$ = 2.462) the mean Milton Keynes aerosol $^{208}Pb/^{207}Pb$ composition of 2.380 is achieved (Figure 3.11). This indicates that it is possible to achieve Milton Keynes aerosol compositions by mixing vehicle emissions and urban regolith-derived particles.

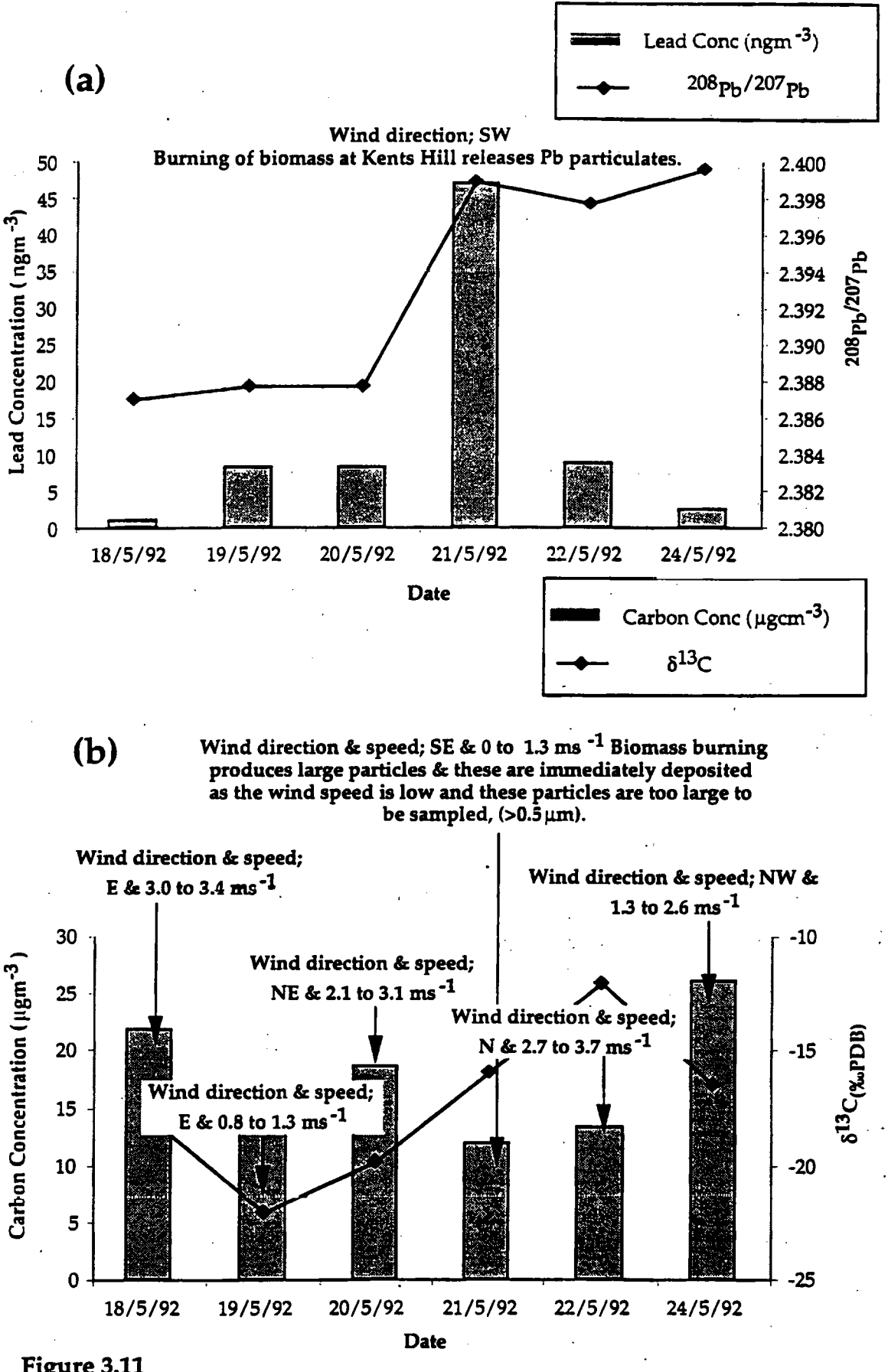

Figure 3.11
C and Pb concentration and isotopic values for the May 1993 Milton Keynes data are related to weather conditions; (a) Pb concentration and isotopic composition data is associated with wind direction and rain, (b) C concentration and isotopic composition data is associated with wind speed.

5th to 26th November, 1992

Carbon and Pb concentrations remained steady throughout the week, with a mean of 29.45 μg cm^{-3} and 9.2 ng m^{-3}, respectively (Figure 3.12). A peak in Pb concentration of 44.0 ng m^{-3} on the 24/11/92 coincided with a particularly gusty day, with wind speeds of 2.2 to 3.6 ms^{-1} and gusts of 6 ms^{-1}. This pattern of high wind speeds and increasing Pb and carbon concentration was observed throughout the year (Table 3.6).

Table 3.6

Tabulated wind directions and carbon and Pb concentrations for days with wind speeds greater than 2 ms^{-1}.

Date	4/2/92	5/2/92	25/5/92	9/10/92	24/11/92
Wind direction & speed (ms^{-1})	West 3.3 to 4.1	West 1.4 to 2.3	North-west 1.3 to 2.6	North-west 2.8 to 3.2	South-west 2.2 to 3.6 (gusts of 6.0)
Pb concentration (ngm^{-3})	34.6	45.0	23.8	4.59	44.0
Carbon concentration (μgcm^{-3})	22.03	37.15	26.01	41.12	31.21

This represents the mechanical process of urban regolith agitation by wind, increasing the input of regolith-derived particles into the atmosphere. Throughout the period 22/11/92 to 26/11/92, the $\delta^{13}C$ varied daily by approximately 2.5 ‰. This variation is thought to represent the influence of asphalting of the surrounding roofs. This occurred on the 23/11/92 (-20.12 ‰), 25/11/92 (-18 ‰) and the 26/11/92 (-17.41 ‰). On these days the $\delta^{13}C$ values are lighter than the intervening days, 22/11/92 (-17.67 ‰) and 24/11/92 (-15.66 ‰). Asphalt would be expected to have a mean $\delta^{13}C$ value of -20 ‰. Therefore, during this sampling week asphalt-derived particles were put into the atmosphere, resulting in isotopically light carbon. The mixing of this isotopically light carbon with the Milton Keynes background aerosol during the intermediate days, produces heavier carbon isotopic signatures. Carbon concentration also increases when asphalting of the roof is in operation (29.07 to 34.16 μg cm^{-3}).

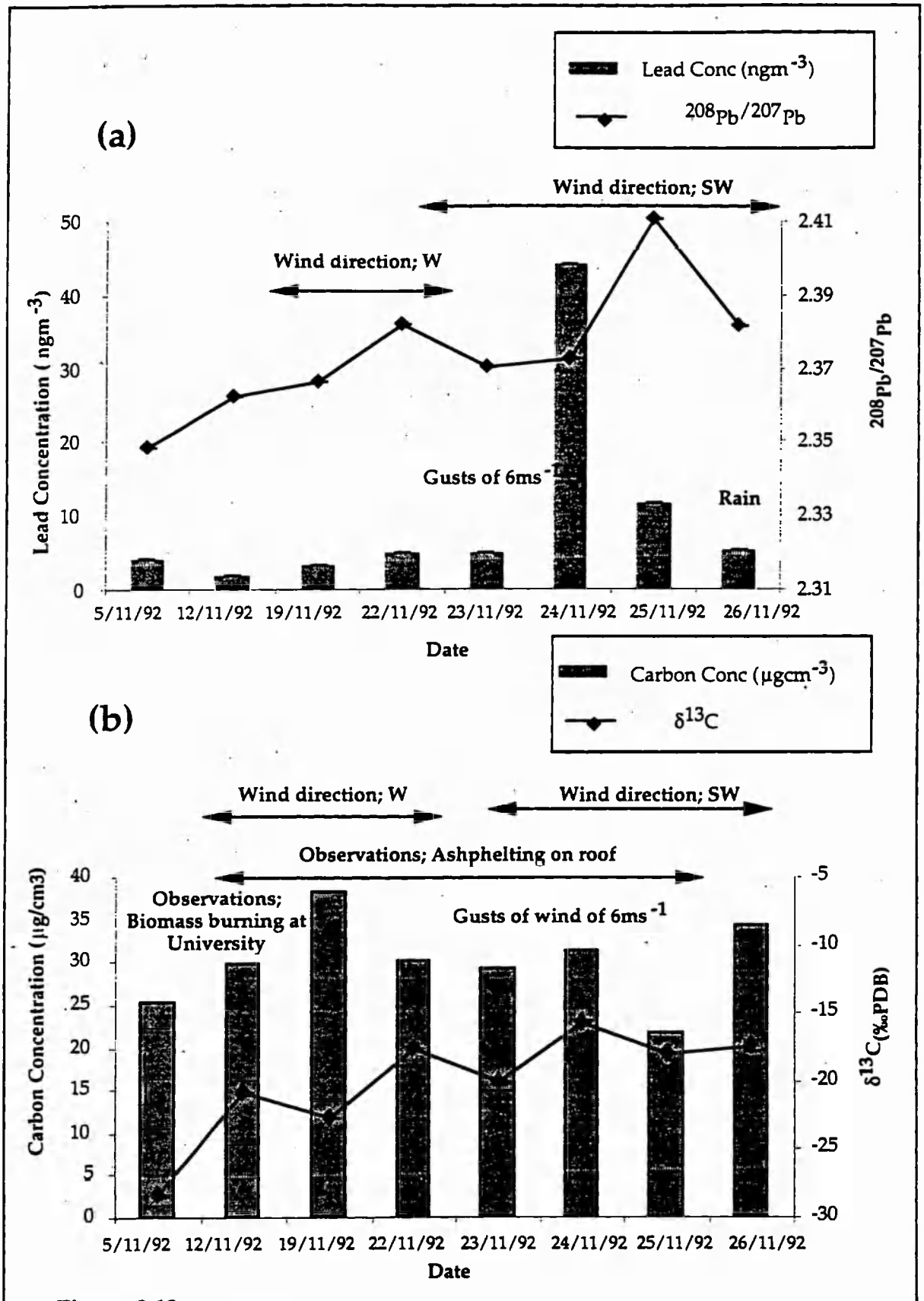

Figure 3.12
C and Pb concentration and isotopic values for the November 1992 Milton Keynes data are related to weather conditions; (a) Pb concentration and isotopic composition data is associated with weather conditions, (b) C concentration and isotopic composition data is associated with wind direction and rain.

The Pb isotopic composition for November (Figure 3.12) are very different to the annual $^{208}Pb/^{207}Pb_{mean}$ of 2.380. These ratios indicate a strong vehicle influence and not urban regolith. It is suggested that during these gusty days, wind may also agitate previously deposited vehicle Pb emission derived particles. This process may result in a shift of Pb isotopic composition. The process may be only one of several wind dependent processes influencing Pb isotopic composition. Therefore, the suggested relationship between Pb isotopic composition and wind speed may well be more complex than first suggested. The relationship may be equally dependent upon the prevailing wind direction.

3rd to 21st December 1992

Carbon concentrations were relatively constant (mean concentration of 32.53 μg cm^{-3}) with a high of 63.08 μg cm^{-3} on 20/12/92 (Figure 3.13) and coincided with asphalting of the surrounding roofs and pungent emissions from the Universal Flavourings factory which produces food flavourings. These two sources are predominantly carbon-producing with little influence expected on Pb concentration. Indeed Pb concentrations were observed to decreased markedly (Figures 3.13). The $\delta^{13}C$ values varied from -12.98 to -17.39 ‰, with daily variations of approximately 2 ‰. Isotopically heavy values of -12.98 ‰ (14/12/92) and -14.48 ‰ (16/12/92), were collected during days when the Universal Flavourings factory was in operation (Figures 3.13). Asphalting of the surrounding roofs occurred on the 15th and 17th of December 1992, these samples exhibiting relatively light $\delta^{13}C$ values of -17.39 and -15.88 ‰, respectively. These light $\delta^{13}C$ values were also recorded on other sampling days when asphalting occurred, for example the 25th ($\delta^{13}C$ of -12.66 ‰) and 26th of November ($\delta^{13}C$ of -15 ‰), and 4/12/92 ($\delta^{13}C$ of -15.99 ‰). Asphalt consists of a mix of organic components primarily of petroleum origin. Asphalt would be expected to exhibit light $\delta^{13}C$ values and may have contributed to the light isotopic component, -12.66 to -15.99 ‰.

The Pb concentration is influenced by wet deposition, for example 15/12/92 to 17/12/92 samples were collected on wet days and exhibited low Pb concentrations of 0.32 to 2.41 ng m^{-3}, respectively (Figure 3.13). Pb isotopic composition also dropped from 2.388 (± 0.0002) on the 14/12/92 to 2.366 (± 0.0002) on the 16/12/92, indicating an increase in a vehicle component. This is in keeping with the hypothesis presented earlier

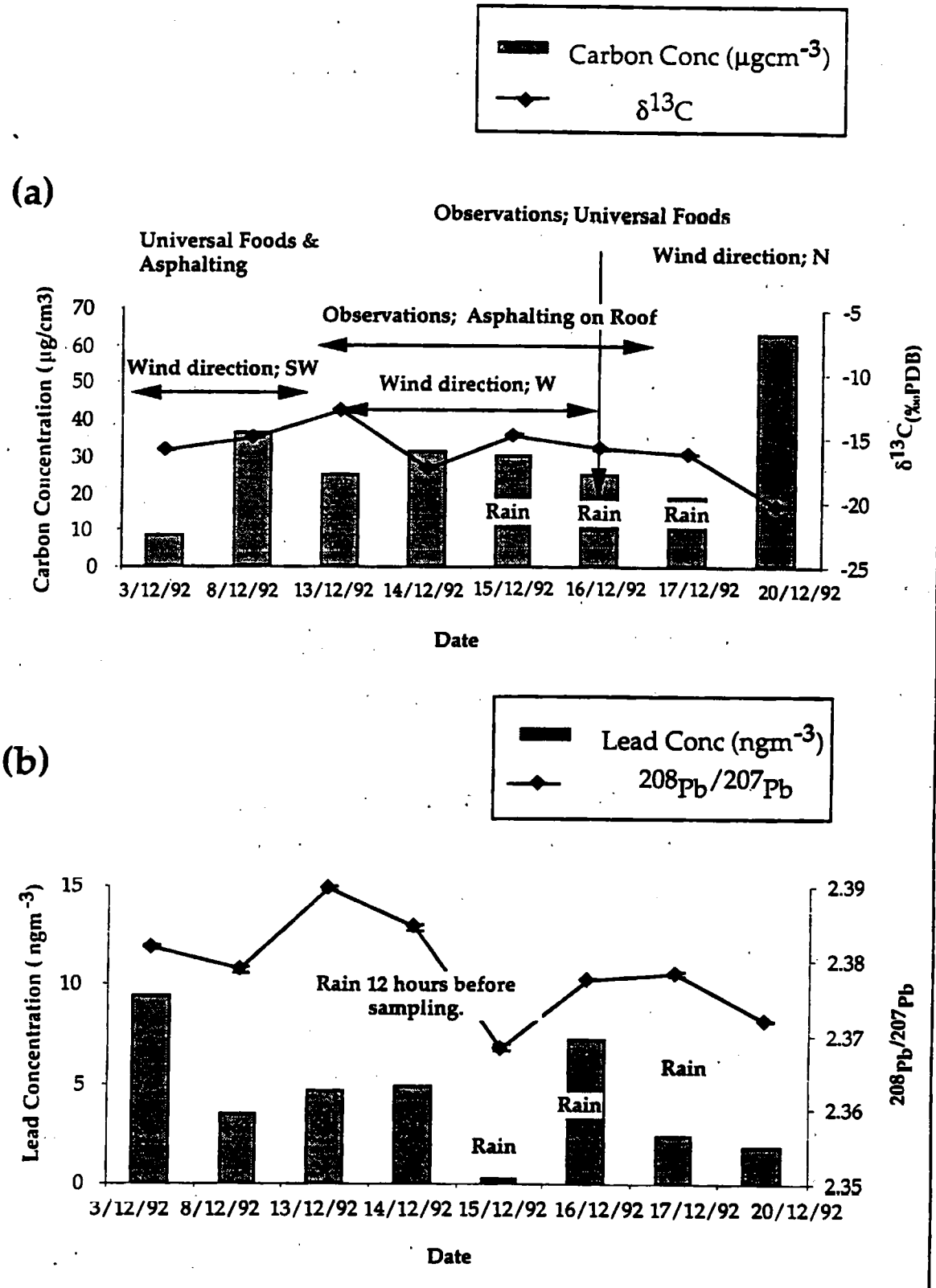

Figure 3.13
C and Pb concentration and isotopic values for the December 1992 Milton Keynes data are related to weather conditions; (a) C concentration and isotopic composition data is associated with wind direction and rain, (b) Pb concentration and isotopic composition data is associated with weather conditions.

that, as Pb particles are washed-out of the atmosphere the immediate input into the atmosphere is vehicle-emissions derived. This juvenile aerosol then matures as it mixes with other sources. This process is depicted during this sampling week.

8th to 29th January 1993

Carbon and Pb concentrations varied from 30.15 to 50.3 $\mu g cm^{-3}$ and 0.02 to 6.41ng cm^{-3} respectively (Figure 3.14). Rain during sample days affected the Pb concentration. For example on the 26/1/93 and 28/1/93 wet days, Pb concentrations were 0.63 ng m^{-3} and 0.06 ng m^{-3} respectively, increasing on dry days (27th, 29th and 30/1/93) to 2.35 ng m^{-3}, 6.41 ng m^{-3} and 3.72 ng m^{-3}, respectively (Figure 3.14). $\delta^{13}C$ values varied from -18.04 to -21.63 ‰ (Figure 3.14). The isotopically light value of -21.63 ‰ (26/1/93) is indicative of an organic source, and coincided with the operation of the university incinerator. The incinerated material (animal remains) would be expected to exhibit the light $\delta^{13}C$ values observed and may have contributed to the light isotopic value. The $\delta^{13}C$ values steadily became heavier during the week indicating the mixing of incinerator-derived particles and background aerosols. The $^{204}Pb/^{207}Pb$ ratios were anomalous to the suggested theory and did not exhibit an increase in a vehicle component during wet days or an urban regolith component on gusty days, as exhibited throughout the year (Figure 3.14). This suggests that there is at least one other Pb source which has not been as yet characterised; for example a long distance source.

Summary of daily variations

For the 4 periods with daily data several similarities have been noted;

(1) Three local carbon sources were identified; asphalt, Universal Flavourings and university incinerator emissions and may be responsible for the variation in $\delta^{13}C$ values.

(2) Wind speed and $^{208}Pb/^{207}Pb$ composition correlated. Relatively high wind speeds, >3 ms^{-1}, increase the input of regolith derived particles (2.462) into the atmosphere producing aerosol $^{208}Pb/^{207}Pb_{mean}$ compositions of 2.416 (± 0.001).

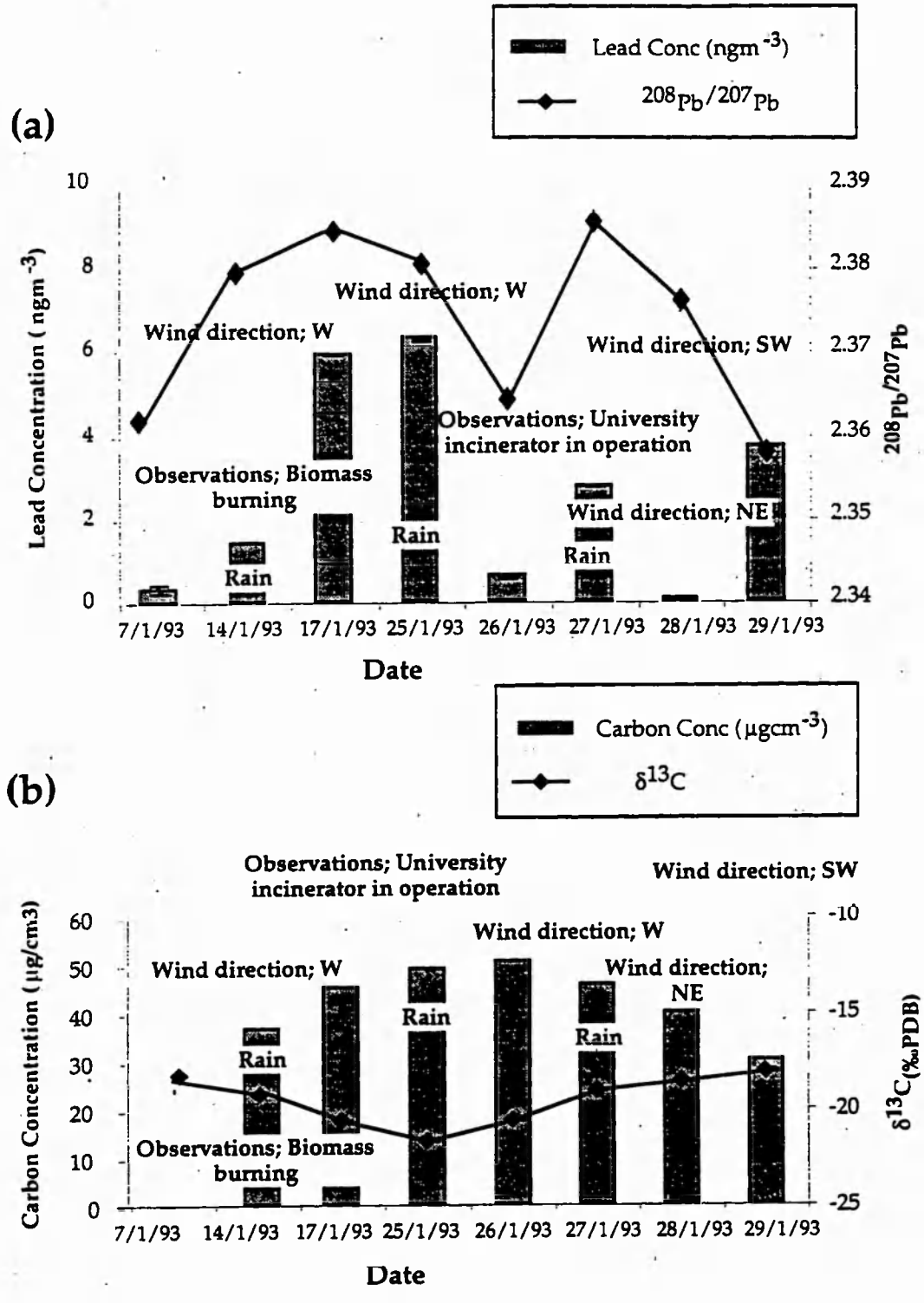

Figure 3.14
C and Pb concentration and isotopic values for the January 1993 Milton Keynes data are related to weather conditions; (a) C concentration and isotopic composition data is associated with wind direction and rain, (b) Pb concentration and isotopic composition data is associated with weather conditions.

(3) Carbon and Pb concentrations, $\delta^{13}C$ values and $^{208}Pb/^{207}Pb$ compositions are thought to be related to rain episodes. This is thought to indicate an urban regolith component, which would be expected to remain relatively constant.

These daily carbon, Pb and weather relationships are reflected and magnified in the annual trends identified from the 1992 and 1993 samples.

3.5 Summary of Milton Keynes data

Overall, the Milton Keynes dataset characterises two distinct sources and indicates that mixing of carbon and Pb particles occurs in this area. In brief, January-September 1992 samples were indicative of a dominant vehicle component and the October 1992-April 1993 dataset may be indicative of a regolith particle component, influenced by a hydrocarbon mixing component ($\delta^{13}C$ values of -13 to -23 ‰ and high carbon concentrations). These samples are thought to be influenced by DERV emissions and urban regolith particle mixing, whereas the January-September 1992 samples are influenced by petrol emissions.

Weather has been found to greatly influence concentration and isotopic composition. It is suggested that rain washes out Pb in the atmosphere. Lead isotopic composition of the aerosol reflects this with the aerosol becoming predominantly influenced by vehicle-emissions-derived particles ($^{208}Pb/^{207}Pb$ ratio of 2.379), which is the "juvenile aerosol". The aerosol then matures by mixing of the juvenile aerosol and other local sources, such as urban regolith particles. As the aerosol matures the Pb concentration increases and the isotopic signature changes to a $^{208}Pb/^{207}Pb$ ratio of 2.389.

3.6 Wales carbon and lead results

The Pb and carbon concentration and isotopic compositions of aerosol samples from Wales were collected and analysed between 1991 and 1993. The data are tabulated by year in Appendix B (vi). Wales 1991 is discussed separately because samples were gathered under different conditions from the 1992 and 1993 samples.

3.6.1 Wales 1991

In 1991 a reconnaissance field trip was organised to ascertain the composition and variation of carbon and Pb atmospheric particles in south Wales. The sample sites chosen represent varied environments (Table 3.7).

Table 3.7

Wales 1991 sample site identification.

Industrial	Cliffs	Beach	Rural Upland
Swansea	Mwnt	Penbryn	Babel
Port Talbot	Molygrove	Parrog	Mean Llea
Milford Haven	Newgale	Abercastle	Mountain centre
Narbeth (Town)		Whitesands	
		Marloes	
		Freshwater East	
		Rhossilli Bay	
		Mumbles (Rocky)	

3.6.1.1 Lead

The Pb concentrations varied from 0.1 ng m^{-3} (± 0.002) at Rhossilli bay to 60.65 ng m^{-3} (± 0.02) at Port Talbot with a mean of 50.67 ng m^{-3} (n = 18). The Pb concentration increases towards the industrial and urban areas and is at a maximum at Port Talbot, an industrial site. Milford Haven (15.6 ng m^{-3} ± 0.01), Swansea (15.8 ng m^{-3} ± 0.07) and Port Talbot (60.65 ng m^{-3} (± 0.02) all exhibit high Pb concentration values, these sample sites being industrial areas. The Pb concentration decreases from to 0.44 ng m^{-3} at Freshwater East to 0.18 ng m^{-3} at Mean Llea and 0.1 ng m^{-3} at Rhossilli bay and then increases again towards Swansea and Port Talbot.

It can be seen from Figure 3.0, that along the coastline, the isotopic composition varies with isotopically low sites being identified, 3 industrial and 1 marine, with a minimum value of 2.2360 (± 0.0001) at Penbryn. The isotopic composition is markedly different at these sites indicating a different source of Pb, this is probably due to an industrial influence at 3 of these sites, Swansea, Port Talbot and Milford Haven (Table 3.8).

Table 3.8

$^{208}Pb/^{207}Pb$ values of the Penbryn, Milford Haven, Port Talbot and Swansea sites.

Location	$^{208}Pb/^{207}Pb$	Standard Error
Penbryn	2.236	0.0005
Milford Haven	2.366	0.0006
Port Talbot	2.376	0.0002
Swansea	2.382	0.0008

The Penbryn site was found to be anomalous. No other satisfactory explanation can be offered for the Penbryn site except that the HBr was contaminated. This theory is substantiated by the low carbon concentration at this site. Figure 3.15 indicates that there is a clear distinction between Penbryn and other sites. Thus, Penbryn has been regarded as a contaminated sample and has not been included in further discussions.

Samples were taken along two transects inland, both from the coast to the Brecon Beacons. The first included Newgale ($^{208}Pb/^{207}Pb$ 2.396), Narbeth ($^{208}Pb/^{207}Pb$ 2.399), Mountain centre ($^{208}Pb/^{207}Pb$ 2.382) and Mean Llea ($^{208}Pb/^{207}Pb$ 2.395). This transect does not indicate any marked change in Pb isotopic composition (Figure 3.0). The second transect included Mwnt ($^{208}Pb/^{207}Pb$ 2.389), Babel ($^{208}Pb/^{207}Pb$ 2.388) and Mountain centre ($^{208}Pb/^{207}Pb$ 2.382). This inland transect also does not indicate any change in isotopic composition. Thus, from this preliminary field study it was concluded that the Pb isotopic composition of aerosol particles did not indicate a change of Pb source from rural to marine areas. However, a marked change in Pb isotopic composition and source of

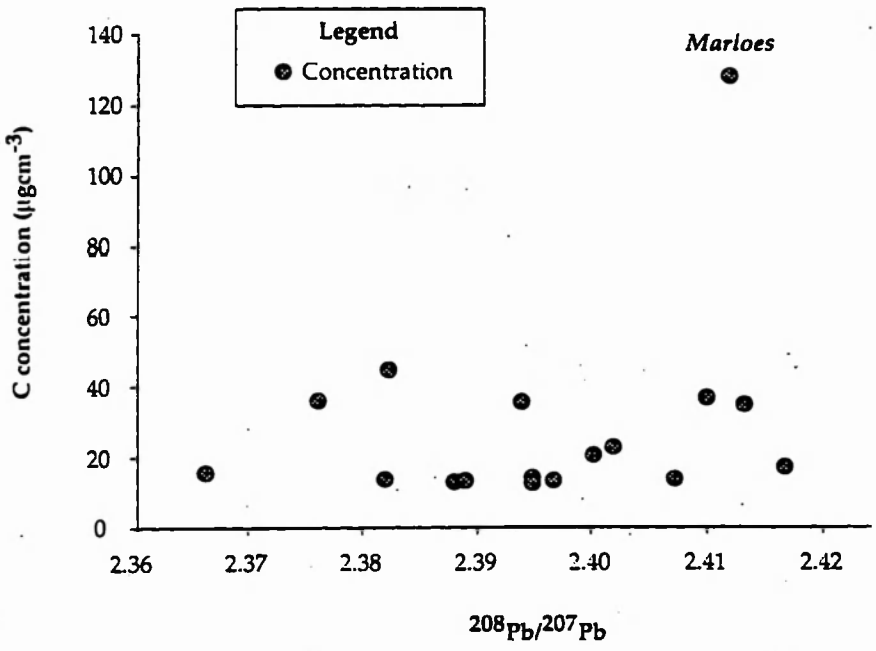

Figure 3.15
The C concentration and $^{208}Pb/^{207}$ Pb composition data for the Wales 1991 sites idicates Penbryn as a contaminated site. The Penbryn sample is not plotted here because it has a contaminated $^{208}Pb/^{207}$ Pb value of 2.236.

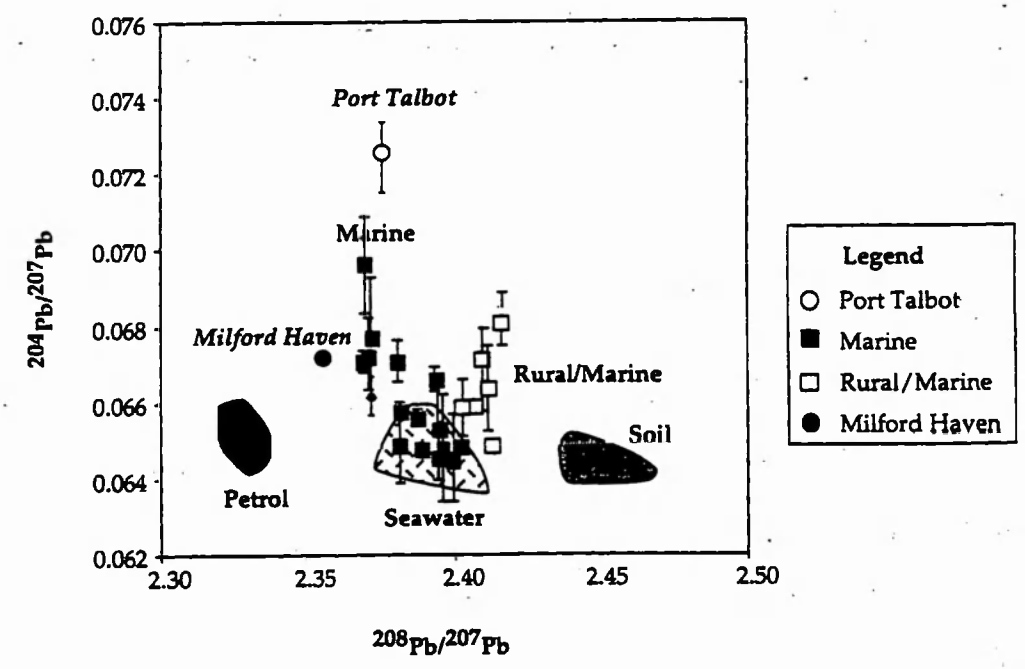

Figure 3.16.
Seawater can be identified by the Pb isotopic compoitions as the direct source of the marine Wales 1991 data. The marine/rural data lie in between the seawater and soil sources, indicating a mix origin of the aerosol. Port Talbot and Milford Haven values do not lie in either group indicating a separate source.

atmospheric particles could be identified along the south Wales coast from mainly marine sources to industrial sources.

When the $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ data values were analysed they indicated 2 distinct marine groups and 4 non-grouped sites (Figure 3.16 and Table 3.9).

Table 3.9

The 1991 Wales sources with Pb isotopic values aerosol particles.

Aerosol	Location	$^{208}Pb/^{207}Pb$	Mean	$^{204}Pb/^{207}Pb$	Mean
Rural/Marine	Narbeth, Mean Llea, Newgale, Rhossilli Bay, Mumbles, Abercastle, Mwnt and Mountain centre	Max. = 2.4129 Min. = 2.382	2.396 (n=7)	Max.= 0.0648 Min.= 0.06414	0.0646 (n = 7)
Marine	Whitesands, Marloes, Newport, Molygrove and Freshwater East	Max. = 2.416 Min. = 2.394	2.408 (n=5)	Max.=0.0678 Min. = 0.0659	0.0665 (n = 5)
Industrial sites	Milford Haven, Swansea, Port Talbot	2.366 (± 0.001) 2.382 (± 0.001) 2.376 (± 0.0001)	n/a	0.0672 (± 0.001) 0.0657 (± 0.0001) 0.0732 (0.001)	n/a
Rural	Babel	2.388 (± 0.0001)	n/a	0.0656 (± 0.0001)	n/a

3.6.1.2 Carbon

$\delta^{13}C$ varies along the Welsh coast from -18.9 ‰ at Swansea to -9.9 ‰ at Freshwater East, with a mean (n=17) of -15.2 ‰. There does not appear to be an identifiable pattern in the variation of $\delta^{13}C$ along the coast in terms of marine or industrial sources (Figure 3.17).

However, when the possible sources are more closely examined, the $\delta^{13}C$ values of the underlying geology of the sites appear to be similar to the aerosol values. This suggests that the different geology gives rise to distinctly different soil types, which in turn favour different vegetation, producing particle $\delta^{13}C$ values. However, it was noted that mean carbon concentration was also dependent upon the proximity to vehicles/car parks and industry (Figure 3.17 and Table 3.10):

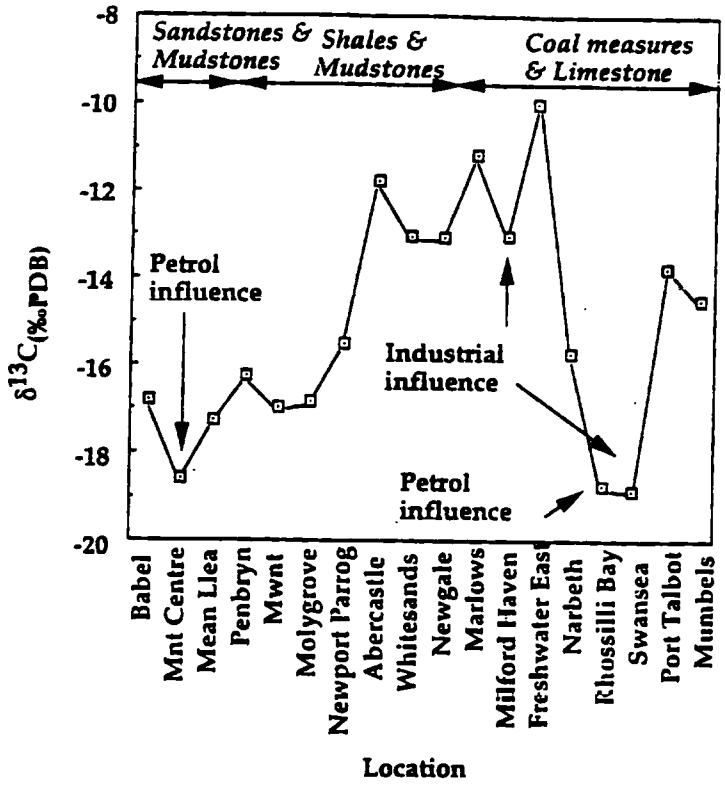

Figure 3.17
The $\delta^{13}C$ values of the Wales 1991 aerosol samples vary with geology and anthropogenic influence.

(a) Mwnt (12.0 μg cm^{-3}), Penbryn (12.7 μg cm^{-3}), Mumbles (21.47 μg cm^{-3}), Mean Llea (12.9 μg cm^{-3}) and Mountain centre (12.3 μg cm^{-3}) all exhibit low carbon concentrations and are representative of areas with no/little vehicle influence.

(b) Narbeth (19.4 μg cm^{-3}) and Molygrove (15.7 μg cm^{-3}) exhibit high carbon concentrations and are indicative of vehicle influence.

(c) Newport Parrog (35.4 μg cm^{-3}) has a small harbour. During sampling diesel outboard motors were periodically started. This is thought to account for the relatively high carbon concentration at this site.

(d) The Marlows sample site is 1.5 km from a busy National Trust car park. In addition, a group of divers arrived during sampling and used a dinghy with an outboard motor, which produced a visible output of black smoke for some 20 minutes. (127.2 μg cm^{-3}).

Table 3.10

The geology and soil conditions of sample sites, with identified flora. The different habitats produce different flora with distinctive $\delta^{13}C$ values.

Location	$\delta^{13}C$ (‰PDB)	Geology	Soil Conditions	Vegetation
Babel, Mountain Centre and Mean Llea.	-16.3 -18.6 -17.3	Mudstones and sandstones.	Acidic soils, with some vehicle hydrocarbon input.	*Erica* spp. (Heathgrass), *Ulex europaeus* (Gorse) and *Cytisus* spp. (Broom).
Narbeth.	-15.8	Black Shales.	Organic rich/ Acidic soils.	Town (grasses)
Penbryn, Mwnt, Molygrove and Newport.	-16.3 -17.0 -16.9 -15.5	Calcareous Flags and Goodwick shales.	Cliffs with alkaline soils.	*Agropyron pungens* (Sea couch), *Armeria maritima* (Thrift), *Matthiola* spp. (Stocks) and *Scilla* spp. (Squills).
Abercastle and Marlows.	-11.8 -11.2	Shales	Organic rich/ Acidic soils.	*Armeria maritima* (Thrift) and *Matthiola* spp. (Stocks).
Whitesands and Newgale.	-13.1 -13.5	Mudstones, Sandstones and acid tuffs.	Acidic soils.	*Festuca rubra and F. ovina* (Red/Sheep fescue), *Agropyron junceiforme* (Sand couch), *Astragalus danicus* (Purple milk vetch) and *Blackstonia perfoliata* (Yellow wort).
Milford Haven , Mumbles and Port Talbot.	-13.1 -14.6 -12.8	Coal measures and Limestone.	Organic rich soils with some anthropogenic influence.	*Glaux maritima* (Sea milkwort), and *Halimone portulacoides* (Sea purslane).
Rhossilli Bay and Swansea.	-18.8 -18.9	Sandstones, Shales and Coal measures.	Organic rich soils, with some vehicle hydrocarbon input.	*Anagallis tenella* (Bog pimpernel) and *Calystegia soldanella* (Sea bindweed). Town.
Freshwater East	-9.9	Limestone.	Alkaline soils.	*Rubus caesius* (Dewberry) and *Iris pseudacorus* (Yellow iris).

(e) Swansea (43.41 μg cm^{-3}) and Port Talbot (34.7 μg cm^{-3}) are both industrial areas, with many anthropogenic sources of carbon. The $\delta^{13}C$ value of -18.93 ‰ for Swansea is indicative of hydrocarbon sources, such as petrol. The Port Talbot $\delta^{13}C$ value of -13.8 ‰ is clearly different and is thought to indicate an unknown industrial source.

(f) Milford Haven is an industrial town with an Esso oil refinery in close proximity. Carbon concentration would be expected to be high, but paradoxically it is not. In fact, it is relatively low (14.4 μg cm^{-3}).

Lead concentration also indicates a distinction between marine and industrial sources (Table 3.11). Carbon concentration for urban sites have not been found to be greater than for the marine sites. In the United Kingdom the concentration of PM_{10} is thought to be fairly consistent (Harrison and Jones,1995). During the summer secondary particulates produced by chemical reactions are generated whilst in winter PM_{10} concentration are thought to reflect direct traffic source emissions (QUARG,1993).

Table 3.11

Mean, maximum and minimum values of lead and carbon industrial and marine groups.

Group	Concentration	Location
Marine		
$Pb_{maximum}$	0.6 ng m^{-3}	Molygrove
$Pb_{minimum}$	0.1 ng m^{-3}	Rhossilli Bay
Pb_{mean}	0.3 ngm^{-3}	
$C_{maximum}$	35.4 μg cm^{-3}	Newport
$C_{minimum}$	11.2 μg cm^{-3}	Abercastle
C_{mean}	31.6 μg cm^{-3}	
Industrial Marine		
$Pb_{maximum}$	60.7 ng m^{-3}	Port Talbot
$Pb_{minimum}$	15.6 ng m^{-3}	Milford Haven
Pb_{mean}	38.1 ng m^{-3}	
$C_{maximum}$	43.4 μg cm^{-3}	Swansea
$C_{minimum}$	14.4 μg cm^{-3}	Milford Haven
C_{mean}	30.8 μg cm^{-3}	

3.6.1.3 Discussion

From this preliminary study it was established that it is possible to distinguish source areas for carbon and Pb by using concentration and isotopic composition of aerosol particles.

Generally Pb concentration is low with a mean value of 0.34 ng m^{-3}. The concentration increases towards industrially-influenced sites such as Milford Haven (15.6 ng m^{-3}) and Port Talbot (60.7 ng m^{-3}). This is mirrored by $^{208}Pb/^{207}Pb$ compositions which decrease greatly at industrial sites. Thus, the $^{208}Pb/^{207}Pb$ compositions and Pb concentration for the sample sites in 1991 are negatively related (Table 3.12).

Lead isotopic compositions indicate the existence of 2 distinct sources of marine Pb particles and the uniqueness of the 3 industrial sites (Figure 3.16 and Table 3.12).

Therefore, by coupling Pb parameters, industrial and marine sites can be characterised (Figure 3.16). However, no significant Pb concentration or isotopic change could be identified in the marine/rural transects in terms of Pb concentration and/or isotopic composition.

Table 3.12.

The Pb concentration, $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ ratio values of industrially-influenced sample sites.

Location	Pb concentration (ng m^{-3})	$^{208}Pb/^{207}Pb$	$^{204}Pb/^{207}Pb$
Milford Haven (n= 3)	15.6 (± 0.09)	2.366 (0.001)	0.0672 (0.001)
Swansea (n= 3)	15.8 (± 0.01)	2.382 (0.001)	0.0658 (0.0001)
Port Talbot (n= 3)	60.7 (± 0.02)	2.376 (0.001)	0.0732 (0.001)

Lead and carbon concentrations indicate two groupings of sites: Marine (Pb concentration 0.01 to 0.06 ng m^{-3}; carbon concentration 11.2 to 35.4 μg cm^{-3}) and Industrial (Pb concentration 1.6 to 6.1 ng m^{-3}; carbon concentration 14.4 to 43.4 μg cm^{-3}). This supports the premise that aerosols can be used to identify the number of carbon and Pb sources within the atmosphere in a particular region. The sample $\delta^{13}C$ values indicate a relationship between vegetation, soil and the underlying geology. It is suggested that the $\delta^{13}C$ values

vary with plant community type (Table 3.10 and Figure 3.17). For example, marine, sandstone, sandy sites general produce nutrient-poor acidic soils. Upon these typically dune environments slack/mobile dune habitats are common. Dune habitats give rise to plant communities such as sand couch, purple milk vetch and yellow wort which all flourish in acidic sandy soil conditions. For example, Newgale and Whitesands exhibit $\delta^{13}C$ values of -11 ‰ and -13.5 ‰, respectively. A contrasting example of plant communities and $\delta^{13}C$ values is found on the rocky cliffs of Penbryn, Mwnt, Molygrove and Newport Parrog. Here, there is a thin calcareous soil which supports a short and rugged plant community. This includes flora such as sea couch, thrift, stocks and squills, producing lighter $\delta^{13}C$ values of -15.5 to -17.0 ‰. No correlation between plant habitat and Pb isotopic composition was identified.

High Pb concentrations occur in industrial areas such as Port Talbot. The $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ isotopic compositions indicate that three sources can be distinguished for the sample sites; the two industrial sites of Port Talbot and Milford Haven being markedly different from the groups identified (Table 3.13 and 3.14).

Table 3.13

Lead source areas and isotopic compositions

Sources	$^{208}Pb/^{207}Pb$	$^{204}Pb/^{207}Pb$
Rural/marine	**Max = 2.413** **Min = 2.382** Mean = 2.396	**Max = 0.0648** **Min = 0.0642** Mean = 0.0646.
Marine	**Max = 2.416** **Min = 2.346** Mean = 2.408	**Max = 0.0678** **Min = 0.0628** Mean = 0.0665

Pb isotopic composition has been found to be of significance in identifying separate marine source emissions and to distinguish between naturally derived marine sources and anthropogenic sources.

Table 3.14.

Lead industrial source areas and isotopic compositions for the Wales 1991 samples.

Sources	$^{208}Pb/^{207}Pb$	$^{204}Pb/^{207}Pb$
Milford Haven	2.366 (±0.001)	0.0672 (± 0.0001)
Port Talbot	2.376 (±0.0002)	0.0732 (± 0.001)
Swansea	2.382 (± 0.001)	0.0657 (± 0.001)

3.7 Wales 1992 and 1993 results

The preliminary sampling regime of 1991 was followed by specific site sampling in 1992 and 1993. This sampling regime was intended to further characterise source areas and evaluate the influence of weather conditions. The sites were:

(1) Broadhaven (marine).

(2) Rhoscrowther (industrially-influenced marine).

(3) Mean Llea (rural).

(4) Port Talbot (industrial).

(5) Swansea (urban/marine).

3.7.1 Carbon and lead concentrations

The carbon and Pb concentrations ranged from 22.5 to 68.9 μg cm^{-3} and 0.01 to 16.0 ng m^{-3} (n = 62) respectively (Appendix B(vi)). These carbon concentrations are similar to measurements by Brémond *et al.*, (1988) and Heintzberg and Winkler (1984). The carbon and Pb concentrations indicate 3 broad groupings of the samples (Figure 3.18).

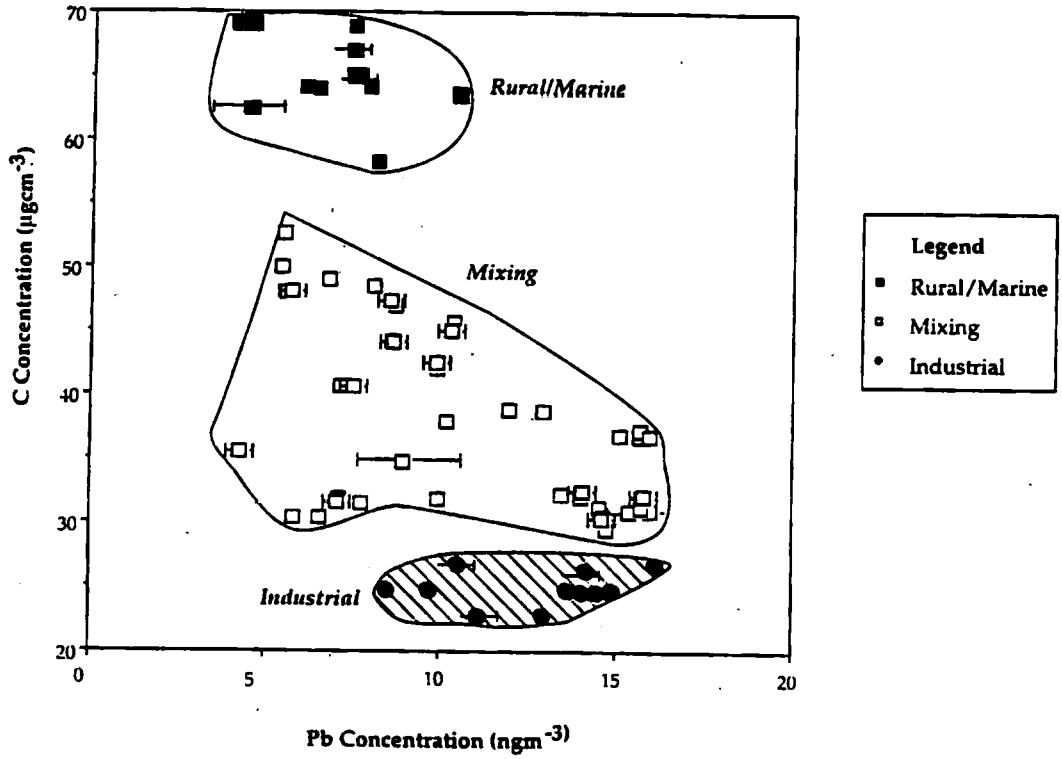

Figure 3.18
Pb and C concentration data identify 3 seperate groups; (1) marine/rural, (2) mixing and (3) industrial.

These groupings are distinct in carbon concentrations but appear to have broad Pb concentrations:

(1) Mean Llea, Rhoscrowther and Broadhaven: Pb concentration 0.1 to 7 ng m^{-3} and carbon concentration 61 to 69 µg cm^{-3}.

(2) Swansea and Port Talbot; Pb concentration 0.5 to 16 ng m^{-3} and carbon concentration 22.5 to 28 µg cm^{-3}.

(3) Mix; Pb concentration 1 to 9 ng m^{-3} and carbon concentration 30 to 46 µg cm^{-3}.

The Mean Llea, Rhoscrowther and Broadhaven high carbon groups represent the rural and marine sites. Two industrial locations, Swansea and Port Talbot, exhibit the maximum Pb concentrations of 15.0 and 16.0 ng m^{-3}, respectively, and low carbon concentrations of 22.5 and 30.14 μg cm^{-3}. Carbon concentration is thought to be affected by weather conditions. This relationship is most clearly identified in the Mean Llea and mixed groups. On dry days (15/3/92, 25/2/93 and 27/2/93) carbon concentrations are high and on wet days (14/3/92 and 16/3/92) carbon concentrations are low. High carbon concentration on dry days is probably due to the incorporation of mechanical breakdown of vegetation and soil particles. This reflects weather conditions, the variation of carbon sources output and their incorporation into the aerosol.

However, Pb concentration is not distinct. This may be related to the mix of Pb sources (point sources = industrial and linear = vehicles) which inject Pb particles into different levels of the troposphere. Thus it would be expected that Pb particles injected high into the troposphere will be transported further than local ground-level vehicle emissions. Therefore the different transportation mechanisms and waether may account for the lack of Pb concentration resolution.

3.7.2 Carbon concentration and $\delta^{13}C$ values

The majority of the samples have $\delta^{13}C$ values of >-22 ‰, in fact only 3 samples, from Mean Llea and Port Talbot, have a $\delta^{13}C$ <-22 ‰ (Figure 3.19 and Appendix B (vi)). The $\delta^{13}C$ values <-22 ‰ all have associated low carbon concentrations, < 30 μg cm^{-3}.

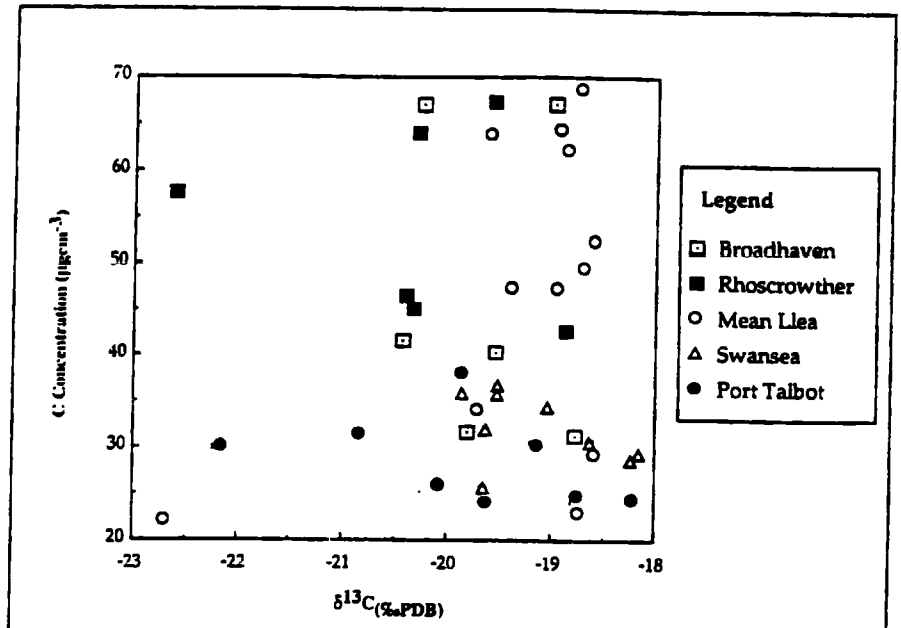

Figure 3.19.
C concentration and isotopic composition data for 1992 and 1993 indicates that only Port Talbot, an industrial site $\delta^{13}C$ values exibit the greatest C variation.

Carbon deposition processes and concentration within the aerosol are related to wet deposition. For example, all of the low concentration samples were collected on wet days and the high concentration samples taken on dry days. Therefore, in order to use carbon concentration as a characterising criterion, all the samples would have had to be collected on days of similar weather conditions. The $\delta^{13}C$ values are also affected by wet deposition, for example Port Talbot $\delta^{13}C$ values of <-22 ‰ all have low carbon concentrations, <30 $\mu g\ cm^{-3}$. Therefore, it is suggested that during wet days there are different carbon sources than on dry days or fractionation occurs during wet deposition.

The $\delta^{13}C$ values and carbon concentrations of each of the 5 sample sites are indistinguishable for 1992 and 1993. It is possible that the carbon sources have remained similar at these sites for both years with a mean 4 ‰ difference (-22 to -18 ‰). There appears to be some difference between the mean total C concentration 1992 and 1993 values. However, this distinction is not sufficient to characterise the sample sites. This poor distinction indicates that the carbon source(s) are relatively constant.

A combination of the $\delta^{13}C$ values and carbon concentration variables produce a separation of the data based mainly upon concentration, which as stated earlier may not be reliable. Thus, these groupings are tenuous and need to be substantiated by larger datasets and/or by statistical analysis.

3.7.3 Isotopic compositions

Broadhaven 1992 and 1993 sample values are different in $^{208}Pb/^{207}Pb$ ratios (Figure 3.20). The values for 1992 ($\delta^{13}C$ values = -18.9 ‰ (± 0.06) to -19.8 ‰ (± 0.04) and $^{208}Pb/^{207}Pb$ = 2.409 (± 0.0002) to 2.412 (± 0.0004), with a mean (n = 7) $\delta^{13}C$ value of -19.4 ‰ (± 0.05) and $^{208}Pb/^{207}Pb$ = 2.411 (± 0.0003), respectively) and 1993 ($\delta^{13}C$ values = -18.8 ‰ (±0.04) to -18.9 ‰ (± 0.02) and $^{208}Pb/^{207}Pb$ of 2.346 (± 0.0004) to 2.411 (± 0.003), with a mean (n = 4) $\delta^{13}C$ value of -19.2 ‰ (± 0.01) and $^{208}Pb/^{207}Pb$ = 2.365 (± 0.001), respectively). The $\delta^{13}C$ values for 1992 and 1993 indicate there are two sources of carbon. The 1993 Broadhaven values display broad $\delta^{13}C$ compositions which are distinct from both Broadhaven 1992 and Rhoscrowther samples ($\delta^{13}C_{mean}$ values of -19.9 ‰ and a $^{208}Pb/^{207}Pb_{mean}$ ratio of 2.415). This probably indicates that the 1992 data represent marine derived particles and that the 1993 data represent the influence of vehicle emissions. Rhoscrowther samples also indicate marine and vehicle emission derived particles.

The Swansea 1992 (-18.6 (± 0.09) to -19.6 ‰ (± 0.01)) and 1993 (-18.2 ‰ (± 0.06) to -19.8 ‰ (± 0.02)) $\delta^{13}C$ values and $^{208}Pb/^{207}Pb$ compositions (2.338 (± 0.0001) to 2.393 (± 0.001) and 2.382 (± 0.001) to 2.410 (± 0.002), respectively) are distinct and indicate 2 different sources (Figure 3.20).

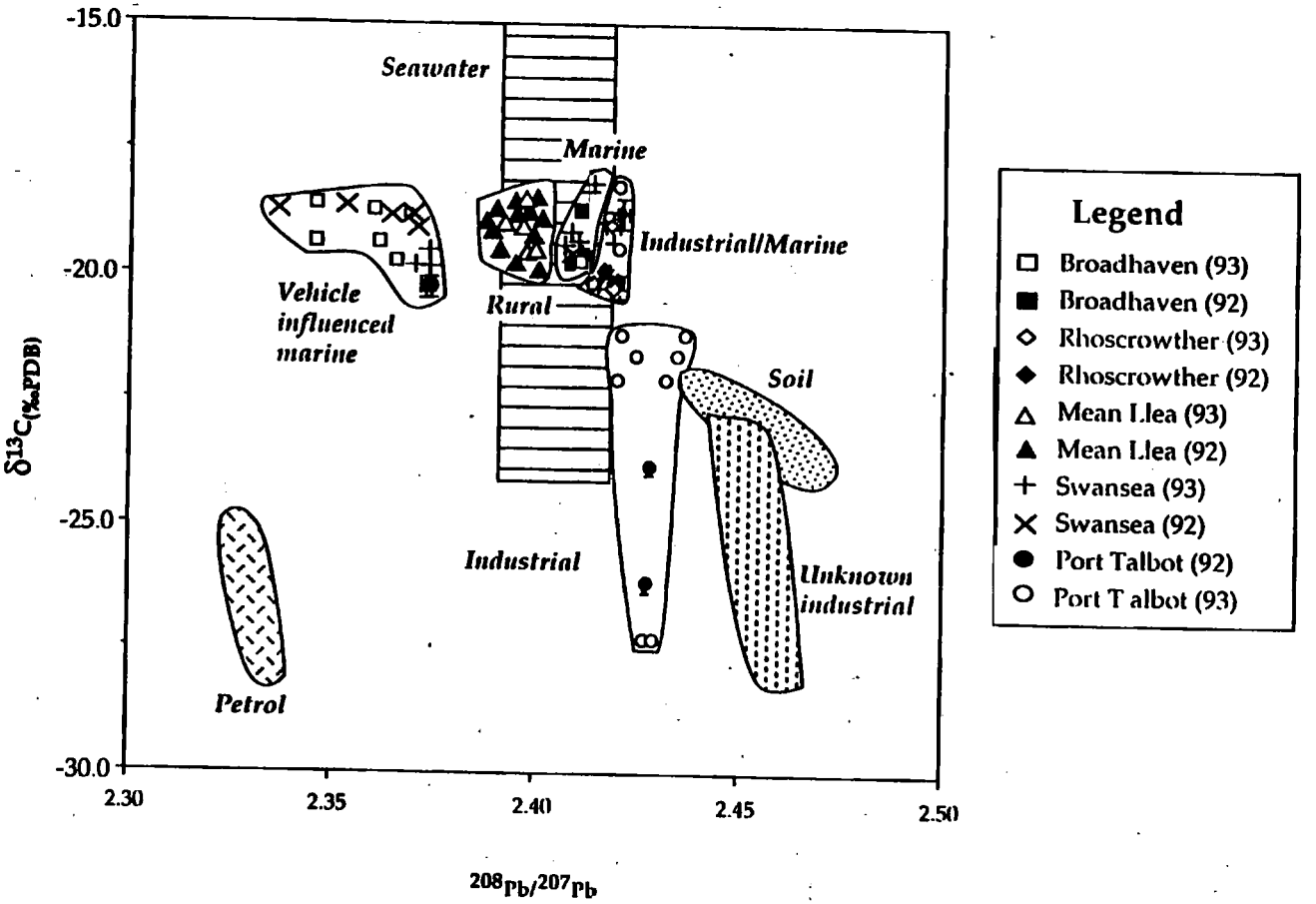

Figure 3.20.
$\delta^{13}C$ values and $^{208}Pb/^{207}Pb$ compositions for 1992 and 1993 samples indicate that source areas of C and Pb are identifiable; vehicle influenced marine, rural, marine industrial and industrial/marine. *Note.*Marine $\delta^{13}C$ values represent marine organic carbon, -2 to -24.5‰ (Hoefs, 1987).

The Port Talbot 1992 $\delta^{13}C$ values -20.3 ‰ (± 0.01) to -26.4 ‰ (± 0.07) and $^{208}Pb/^{207}Pb$ compositions of 2.373 (± 0.0003) to 2.387 (± 0.0001), with 1993 values ranging from $\delta^{13}C$ values of -18.3 ‰ (± 0.01) to -27.4 ‰ (± 0.05) and $^{208}Pb/^{207}Pb$ compositions of 2.420 (±†0.0007) to 2.436 (± 0.0003). Thus, the two years are distinct, with probably the 1992 values representing marine and vehicle emissions-derived particle mixing (see mixing models below) and 1993 values may be attributed to two unknown sources, probably industrial. These unknown industrial emision sources are discussed as X ($^{208}Pb/^{207}Pb = 2.45$ and $^{204}Pb/^{207}Pb = 0.0665$) and Y ($^{208}Pb/^{207}Pb = 2.425$ and $^{204}Pb/^{207}Pb = 0.0641$). However, it must be stated that these results could be due to the spot sampling approach and/or mixing processes.

From the $\delta^{13}C$ values and $^{208}Pb/^{207}Pb$ isotopic ratio data 3 distinctive groupings of the data plus 2 mixing zones can be characterised (Figure 3.20, Table 3.15 and Appendix B (vi)).

Table 3.15 suggests that there are 2 natural sources, marine and rural. Mean Llea values are clearly distinct and no Mean Llea samples fall into any other group. This suggests that there is either one constant and unique Pb source for this sample site (which is not influenced by any other site) or that there is a constant 'cocktail' of sources. The marine group consists of Broadhaven and some of the Swansea samples. This group represents background marine aerosols with little or no vehicle emission influence, with mean sample values similar to the Broadhaven seawater $^{208}Pb/^{207}Pb_{mean}$ of 2.394. The Swansea samples fall into both the marine and vehicle influenced marine group. The samples are wind direction dependent.

Table 3.15

Lead and carbon source areas and isotopic compositions.

Source	Location	$\delta^{13}C_{mean}$ values	$^{206}Pb/^{207}Pb$ mean	$^{208}Pb/^{207}Pb$ mean
Rural	Mean Llea	-19.0 ‰	0.0660	2.40
Industrial	Port Talbot	-23.5 ‰	0.0647	2.427
Marine	Broadhaven and Swansea	-18.9 ‰	0.0646	2.409
Vehicle influenced marine	Broadhaven 1993 Swansea and Port Talbot 1992	-19.7 ‰	0.0647	2.369
Industrial/ Marine	Rhoscrowther and Port Talbot	-21.6 ‰	0.0648	2.417

The industrial group consists of Port Talbot samples which are thought to represent the influence of refinery-derived hydrocarbon particles ($\delta^{13}C$ value of -25 to -28 ‰). The Pb isotopic signatures of the oil refined at this site are not known but the ratios measured in this group are high and indicate a distinctive and discrete Pb source. Therefore, it may be tentatively stated that the carbon and Pb particles in this group are associated and may be attributed to hydrocarbon combustion. The hydrocarbons may originate from refinery particles released in flue gases or a local power station. However, this hypothesis remains speculative, as both the refinery and power-generating companies declined to comment upon the origins of their fossil fuels.

The industrial marine group consists of Rhoscrowther and Port Talbot samples. This group lies between the marine and industrial groups. This group is thought to represent the mixing of industrial and marine-derived particles. Appendix V contains the theoretical mixing models 2c and 2d of Swansea seawater-derived particles ($^{208}Pb/^{207}Pb$ = 2.402 and $^{204}Pb/^{207}Pb$ = 0.0640) and industrially-derived components as end members (Unknown X = $^{208}Pb/^{207}Pb$ 2.445, $^{204}Pb/^{207}Pb$ 0.0665 and Mean Port Talbot = $^{208}Pb/^{207}Pb$ 2.413, $^{204}Pb/^{207}Pb$ 0.0664). Figure 3.21 represents the theoretical mixing models of the industrial components X, Y and Z (Models 3c and d). The Port Talbot and Rhoscrowther samples of this group represent a mixing of marine and industrial Pb particles (Appendix (V)). This model indicates that this grouping is theoretically achievable.

The vehicle-influenced group consists of predominantly Broadhaven 1993 samples with Swansea and Port Talbot 1992 samples. This group represents marine areas which are influenced by vehicle emissions. Figure 3.21 represents the theoretical mixing of marine and vehicle emissions-derived particles (Models 4a and 4b; Appendix B(V)). These models indicate that this grouping is theoretically achievable.

These groups indicate that carbon and Pb isotopes can indeed be used to identify and distinguish regional aerosol sources: industrial, rural and marine.

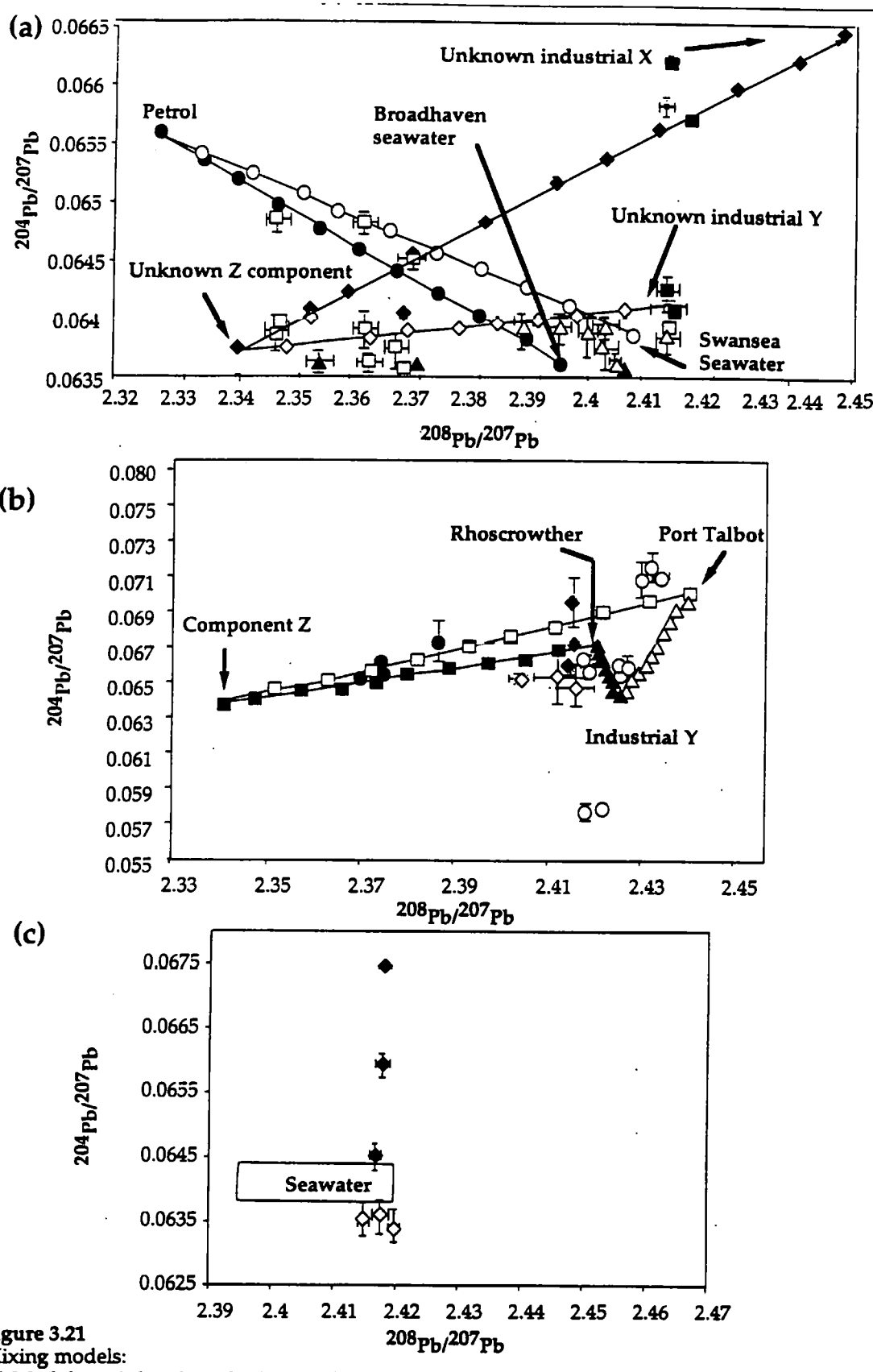

Figure 3.21
Mixing models:
(a) **Models 3c &d and 4a&b.** (Appendix B(v)); a mixing model of Broadhaven (●) and Swansea seawater (○) derived particulates and exhaust-derived aerosols. The Broadhaven 1993 (□) data can be seen to lie within the mixing model end members. Broadhaven 1992 (■), Swansea 1992 (▲) and 1993 (△) data can be explained by the mixing of an unkown component Z and industrial components X (◆) and Y (◇) .
(b) **Models 2g to j.** (Appendix B(v)); a mixing model of Unkown component Z with Port Talbot (□) and Rhoscrowther (■) aerosols and industrial Y with Port Talbot (△) and Rhoscrowther (▲) aerosols. Most of the Rhoscrowther 1992 (◆), 1993 (◇) Port Talbot 1992 (●) and Port Talbot 1993 (○) data lie within the mixing model end members.
(c) Seawater-derived particulates account for the Rhoscrowther 1993 (◇) and one of the 1992 (◆) values. However, some of the 1992 data are not explained by sea water, indicating that the Rhoscrowther aerosol is more complex.

3.7.4 Statistical analysis

3.7.4.1 Factor analysis

In order to further investigate the sources identified in the Wales 1992 and 1993 data a factor analysis was performed. The same calculating conditions as outlined in section 3.4.2 were used.

The Wales 1992 and 1993 samples were analysed separately in order to assess whether an identifiable statistical difference existed between the sampling years.

3.7.4.2 Wales 1992

The factor analysis used 6 variables ($^{208}Pb/^{207}Pb$, $^{204}Pb/^{207}Pb$, $\delta^{13}C$, Pb, carbon concentration and wind direction) with 20 degrees of freedom (Table 3.16).

Three factors were identified;

1. Factor 1 ($^{204}Pb/^{207}Pb$, $\delta^{13}C$, C and Pb concentration). Accounts for 39% of the sample variation.

2. Factor 2 ($^{208}Pb/^{207}Pb$, $^{204}Pb/^{207}Pb$, $\delta^{13}C$, C concentration and wind direction). Accounts for 39% of the sample variation.

3. Factor 3 (Wind direction). Accounts for 22% of the sample variation.

Table 3.16

The factors and factor loadings for the Wales 1992 factor analysis. The level of factor loading significance was taken as >0.5 and are represented in bold type.

Variables	Factor 1 (39% variance)	Factor 2 (39% variance)	Factor 3 (22% variance)
$^{208}Pb/^{207}Pb$	-0.470	**0.650**	-0.330
$^{204}Pb/^{207}Pb$	**0.631**	**0.579**	-0.219
Pb concentration	**0.798**	0.032	0.099
$\delta^{13}C$ values	**0.723**	**-0.549**	-0.110
carbon concentration	**-0.563**	**0.679**	0.046
Wind direction	-0.165	**0.794**	**0.921**

Factor 1 is thought to represent anthropogenic sources with Pb concentration being the important indicator of anthropogenic sources, for example vehicle emission influence.

Factor 2 is thought to represent natural soil/biomass sources, with carbon concentration and wind direction being the important indicators.

Factors 2 and 3 contain wind direction. This component is thought to affect the samples indirectly; For example, wind direction affects the particle transportation mechanisms (Whitby, 1975). Further discussions of the 1992 factor analysis results are conducted in conjunction with 1993 results below.

3.7.4.3 Wales 1993

Again the factor analysis used 6 variables ($^{208}Pb/^{207}Pb$, $^{204}Pb/^{207}Pb$, $\delta^{13}C$, Pb and carbon concentration and wind direction) with 20 degrees of freedom (Table 3.17).

Three factors were identified;

1. Factor 1 ($^{208}Pb/^{207}Pb$, $^{204}Pb/^{207}Pb$, $\delta^{13}C$ and wind direction). Accounts for 40% of the sample variation.

2. Factor 2 (Pb concentration). Accounts for 34% of the sample variation.

3. Factor 3 (carbon concentration and wind direction). Accounts for 26% of the sample variation.

Table 3.17

The factors and factor loadings for the Wales 1993 factor analysis. The level of factor loading significance was taken as >0.5 and are represented in bold type.

Variables	Factor 1 (40% variance)	Factor 2 (34% variance)	Factor 3 (26% variance)
$^{208}Pb/^{207}Pb$	**0.704**	0.112	-0.23
$^{204}Pb/^{207}Pb$	**0.934**	-0.088	-0.140
Pb concentration	0.147	**0.904**	0.156
$\delta^{13}C$ values	**-0.701**	0.102	**0.556**
carbon concentration	0.325	-0.425	**0.699**
Wind direction	**0.507**	0.159	**0.567**

The 1993 samples have an apparent relationship between Pb isotopic compositions, $\delta^{13}C$ and wind direction, with carbon concentration also being related to wind direction in another factor. However, Pb concentration is found to be independent of wind direction. The identification of two wind direction-dependent factors are indicative of the isotopic values of the Broadhaven, Swansea and Port Talbot 1993 samples, which were found to be wind direction-dependent.

Swansea values are an example of wind direction dependent sources with two distinct groupings of data, indicating two separate Pb sources. The 1993 samples represent northerly wind directions, which have passed over the Bristol channel and accumulated a marine component, $^{208}Pb/^{207}Pb$ ratio of 2.409 and $\delta^{13}C$ values of -18.9 ‰. The 1992 samples predominantly represent south-westerly wind directions, indicating both marine and terrestrial influences. This would produce a mixing of seawater and vehicle emission-derived particles. This hypothesis was supported by modelling (Figure 3.21). The components identified by factor analysis were used as end members in mixing model calculations 4a and b.

Conversely, Port Talbot samples have very different $^{208}Pb/^{207}Pb$ ratios, and $\delta^{13}C$ values between 1992 and 1993 indicating 2 different Pb and carbon sources (Figure 3.22). These samples predominantly represent south-westerly wind directions, indicating both marine and

terrestrial influence. This would produce a mixing of seawater and vehicle emission-derived particles (Figure 3.21, Models 4a and b).

The Port Talbot site is complicated by industrial influences. Unknown components X, Y ($^{208}Pb/^{207}Pb$ = 2.425 and $^{204}Pb/^{207}Pb$ = 0.0641) and Z ($^{208}Pb/^{207}Pb$ = 2.34 and $^{204}Pb/^{207}Pb$ = 0.0638) may have an influence in the 1992 aerosol samples. (Figure 3.21, Models 2f to 2j). The 1993 samples are less complex and indicate strong carbon and Pb industrial influence.

It is suggested that factor 1 represents marine sources, with the carbon and Pb concentrations not being significant in this factor. For example, the concentrations of carbon and Pb in marine sources are low in comparison to those in anthropogenic sources thus, the distinctive marine isotopic signatures will be of greater importance. Factor 2 is thought to represent soil/biomass sources, with carbon concentration being the important indicator. Factor 3 is thought to represent the anthropogenic influence in the region (industry and vehicle emisions).

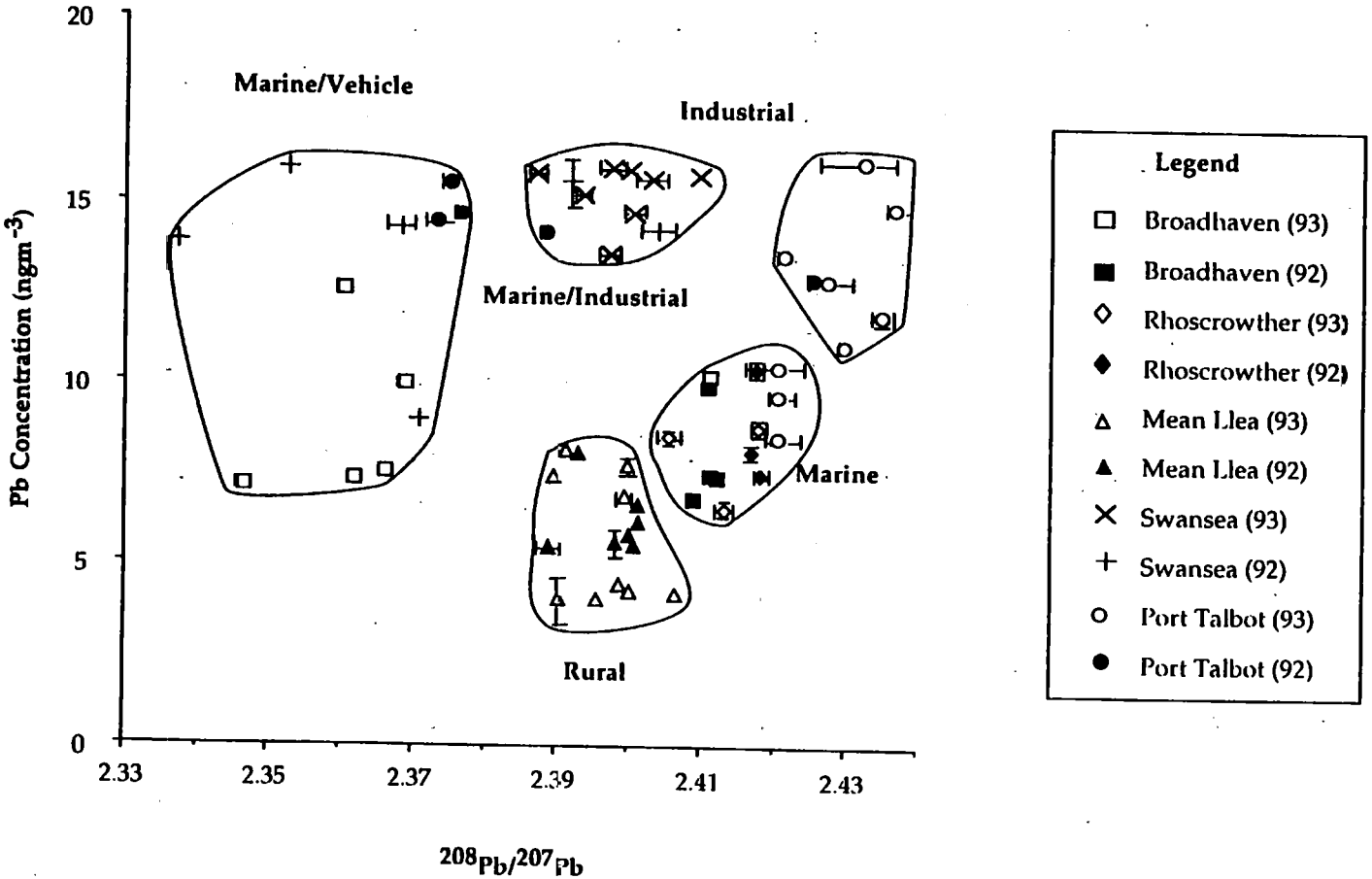

Figure 3.22
Pb concentration and isotopic composition of the 1992 and 1993 samples indicate 3 sources of Pb; marine, industrial and rural, with mixing between these sources.

3.8 Summary

A summary of the Wales 1992 and 1993 sources is given below.

Weather conditions have been found to affect the concentration of both carbon and Pb in the atmosphere. For example, all of the low concentration samples were collected on wet days and the high concentration samples taken on dry days. The high carbon concentration on dry days is most probably due to the incorporation of mechanical breakdown products of vegetation and soil particles. This reflects both the variation of carbon source outputs and their incorporation into the aerosol. The $\delta^{13}C$ values are also affected by wet deposition, for example Port Talbot $\delta^{13}C$ values of <-22 ‰ all have low carbon concentration, <30 $\mu g\ cm^{-3}$. Therefore, it is suggested that during wet days there is a different balance of carbon sources than on dry sample days, or that wet deposition affects fractionation.

There are consistently high Pb concentration values at industrial sites and consistently low concentrations at the rural site. This is thought to indicate that at Swansea and Port Talbot, Pb concentrations are independent of weather conditions. This may reflect a constant output of Pb (vehicle and industrial emissions) at these sites. The carbon and Pb isotopic dataset is discussed in detailed sections below. Thus, Pb output at these sites may "mask" the effect of wet deposition.

The implementation of PCA indicated that wind direction has an effect on carbon concentration and Pb isotopes in the 1992 samples. Lead concentration and isotopic composition were found to be affected by separate factors, indicating that there is more than one component influencing carbon and Pb in the 1992 samples. The three identified factors represent at least two separate sources of carbon and Pb;

(1) Anthropogenic sources with Pb concentration being the important indicator for example, vehicle emission influence.

(2) Natural soil/biomass sources, with carbon concentration being the important indicator.

The 1992 and 1993 factor loadings are similar, it is suggested that there are three main components: marine, soil/biomass and anthropogenic influence. Pb isotopic compositions, $\delta^{13}C$ and wind direction exhibit a relationship, with carbon concentration also being related

to wind direction in another factor. However, Pb concentration is found to be independent of wind direction. The 1992 and 1993 samples are now discussed in greater detail by individual site:

3.8.1 Marine

Rhoscrowther and Broadhaven are both marine sites and are thought to have related atmospheric sources and aerosol compositions (Figure 3.22). This supposition can be substantiated by the Broadhaven 1992 and Rhoscrowther Pb isotopic compositions ($^{208}Pb/^{207}Pb$ mean = 2.411 (± 0.0002) and 2.415 (± 0.0005) and $^{204}Pb/^{207}Pb$ mean = 0.0650 (± 0.0003) and 0.0639 (± 0.0003), respectively).

There is a clear distinction between the Broadhaven 1992 and Rhoscrowther samples and the aerosol isotopic composition of the Broadhaven 1993 samples ($^{208}Pb/^{207}Pb$ = 2.346 (±0.0004) to 2.411 (± 0.003) and $^{204}Pb/^{207}Pb$ = 0.0631 (± 0.002) to 0.0668 (± 0.0003). These values are indicative of separate Pb sources for Broadhaven in 1993 and are related to wind direction. North-westerly winds are samples influenced by a marine aerosol component and are probably responsible for the Broadhaven and Rhoscrowther 1992 sample values. The 1993 samples were subjected to variable wind directions and may be influenced by terrestrial components, such as vehicle exhaust emissions.

3.8.1.1 Rhoscrowther

The Pb concentration varies from 0.02 ng m^{-3} (± 0.003) to 0.54 (± 0.002). The $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ ratios range from 2.415 (± 0.001) to 2.420 (± 0.044) and 0.0630 (±0.0007) to 0.0649 (±0.0008), respectively. 1992 and 1993 samples characterise into two groups. The 1993 samples exhibit relatively large variation in $^{208}Pb/^{207}Pb$ ratios. This has been interpreted as indicating more than one source of Pb influencing this site. This variation is thought to be due to the nature of the site, in close proximity to a Texaco oil refinery and the coast. These sources are dependent upon wind direction. For example, a north-westerly wind direction would be indicative of aerosols originating/transported over marine areas. North-westerly winds produce values close to Broadhaven seawater ($^{208}Pb/^{207}Pb$ =

2.394). Modelling of Pb concentration and isotopic ratios indicate that the mixing of Broadhaven seawater and Rhoscrowther soil produce the sample values for north-westerly winds. This model (Model 6, Appendix B (V)) indicates that the mixing of Broadhaven and Rhoscrowther seawater and soil-derived Pb particles do not produce a Rhoscrowther signature. Thus, both the 1992 and 1993 samples may represent oil refinery influence.

3.8.1.2 Broadhaven

At Broadhaven it was possible to distinguish between 1992 and 1993 Pb sources, indicating that there is more than one source of Pb at this site. Two wind direction-dependent sources of Pb and carbon have been identified for Broadhaven 1992 and 1993 samples, indicating terrestrial (petrol emissions) and marine components:

Source 1

Broadhaven 1993 samples with $^{208}Pb/^{207}Pb$ ratios of 2.34 to 2.370 and $\delta^{13}C$ values of -18 to -19 ‰. The $^{208}Pb/^{207}Pb$ compositions indicate that this is not a single Pb source, but is a mixture of vehicle emissions and marine sources. Figure 3.21 represents the theoretical mixing of marine- and vehicle-derived particles. Models 4a and 4b indicate that these sample values are theoretically achievable by mixing vehicle emissions and marine-derived particles. However, mixing will be dependent on wind direction. The wind direction during sampling was variable north-west to south-west. These wind directions are not influenced by terrestrial components such as vehicle emissions. Thus, this is not a separate Pb source but a mixture of particles derived from marine (2.39) and vehicle (2.33) sources. Since the vehicle emissions source is indicative of terrestrial origin, this mixed aerosol is termed the terrestrial-influenced component.

Source 1 with $^{208}Pb/^{207}Pb$ ratio of 2.338 to 2.371 and Pb concentrations of 0.026 to 1.5 ng m^{-3} encompasses Broadhaven 1993 and Swansea 1992 samples. The wind direction during sampling was variable and the aerosol will have been influenced by terrestrial components, such as leaded petrol driven vehicle emissions. This group exemplifies the susceptibility of marine sites to vehicle emission contamination. This grouping is

substantiated by $\delta^{13}C$ and Pb isotopic compositions (Figure 3.20) which also identifies this group.

Source 2

Broadhaven 1992 samples with $^{208}Pb/^{207}Pb$ ratios of 2.40 to 2.41 and $\delta^{13}C$ values of -18 to -19 ‰, with north-westerly and south-westerly wind directions (marine influenced). This group characterises an uncontaminated marine site with Pb isotope ratios close to that of seawater (Figure 3.20).

For both Pb sources the $\delta^{13}C$ values differentiate into 2 groups with a 1 ‰ difference. This 1 ‰ difference is not thought to be significant because carbon isotope fractionation can easily accommodate such a small isotopic shift, for example, during transportation when particles may be uplifted into the stratosphere and subjected to high temperatures and chemical reactions. Therefore, the carbon source at this site is thought to be constant and most probably of marine origin.

3.8.2 Rural (Mean Llea).

The 1992 and 1993 sample are indistinguishable from each other with Pb concentration from 0.001 to 0.4 ng m^{-3} (Figure 3.22), $^{208}Pb/^{207}Pb$ ratios from 2.372 (± 0.004) to 2.401 (± 0.05) and $^{204}Pb/^{207}Pb$ ratios from 0.0650 (± 0.003) to 0.0677 (± 0.001). The main anthropogenic Pb sources for this site are vehicle emissions-derived particles (Model 5a). Theoretical mixing between Mean Llea soil-derived particles and Broadhaven seawater-derived particles do not produce Mean Llea aerosol values (Model 5b). This vehicle emission influence is the occasional tourist visiting the Neolithic standing stone and Army trucks depositing the odd group for ordinance training. This relationship indicates that for this site there is only one Pb source which varies in concentration and is wind direction independent. The Pb isotopic signature for this site may not be ascribed to simple mixing between soil and petrol-derived particles ($^{208}Pb/^{207}Pb$ ratios of 2.33). This terrestrial source is distinct from the marine Rhoscrowther and Broadhaven sources.

The carbon concentration varies from 64.7 to 68.9 µg cm^{-3}. High carbon concentrations were found to occur on dry days. This is most probably due to the incorporation of

mechanical break-down of vegetation and soil particles. This reflects both variation in output of carbon sources and their incorporation into the aerosol.

3.8.3 Industrial

The Port Talbot and Swansea 1992 and 1993 sample $^{204}Pb/^{207}Pb$ ratios (0.0643 to 0.0707 and 0.0624 to 0.0641, respectively) and $^{208}Pb/^{207}Pb$ ratios (2.344 to 2.373 and 2.338 to 2.410, respectively) cluster into distinct groups indicating more than one Pb source.

3.8.3.1 Port Talbot

The Pb concentration varies from 0.05 (± 0.001) to 16.0 ng m^{-3} (± 0.1). This site displayed the highest Pb concentration of 16.0 ng m^{-3} (3/3/93). The $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ ratios range from 2.373 (± 0.0001) to 2.434 (± 0.004) and 0.0641 (± 0.0002) to 0.071 (± 0.001) respectively. A distinction between 1992 and 1993 Port Talbot samples is apparent (Figure 3.22). This distinction indicates that there is either more than one Pb source at this site for 1992 and 1993 or that the same source has changed in its Pb isotopic composition. It is quite a common occurrence in industry to change supplier. For example, the purchase of coal and Fe ore is generally from the cheapest supplier and this will alter with economic conditions.

The Port Talbot aerosols have also been shown to be affected by the mixing of unknown industrial components Z and Y and petrol emissions-derived particles. Figure 3.21 represents the theoretical mixing models 3a and 3b of unknown industrial components Z and Y and petrol emissions derived particles. These models indicate that this grouping is theoretically achievable. Also, it is not understood why the $^{208}Pb/^{207}Pb$ ratios for the marine/industrial mix group should be higher than the industrial and marine groups. One possible explaination is that an other industrial component may be contributing to this ratio.

3.8.3.2 Swansea

The Pb concentration varies from 0.57 (± 0.003) to 15.0 ng m^{-3} (± 0.03) with $^{208}Pb/^{207}Pb$ and $^{204}Pb/^{207}Pb$ ratios ranging from 2.338 (± 0.0001) to 2.410 (± 0.001) and 0.0624

(±0.0002) to 0.0641 (± 0.0001), respectively. There is a marked division of the Swansea 1992 and 1993 samples. This indicates more than one source of Pb at this site. The 1992 samples exhibit a $^{208}Pb/^{207}Pb_{mean}$ ratio of 2.363 and are thought to be more influenced by vehicle emissions derived Pb particles (2.33). This is a reasonable supposition as the number of leaded petrol-driven vehicles declined during the period of 1992-1993 from 19.57 million tonnes in 1985 to 12.70 million tonnes in 1992. The 1992 samples also exhibit greater Pb isotopic variation (1992 stdev = 0.022) than the 1993 samples (1993 stdev = 0.01). This is thought to be due to the variability of aerosol mixing of marine and vehicle emission particle sources which would be wind-direction dependent. The 1993 samples may be influenced by marine-derived particles (2.394). These samples group tightly in between the 1993 Port Talbot and the Swansea 1992 samples (Figure 3.22). This has been interpreted as an indication that these samples represent a greater dilution of industrially-influenced marine particles, derived either from local industry and/or Port Talbot.

3.9 Conclusion

Carbon and Pb concentration and isotopic compositions are apparently related to weather conditions such as, rain and wind direction. The isotopic data indicated that at Port Talbot and Broadhaven the Pb sources exhibited a temporal variation. The main source components identified by factor analysis were soil, vehicle emissions and weather conditions. Mixing of soil and vehicle emissions-derived particles indicated that the Milton Keynes dataset could be explained by two end-member mixing sources. Rain washout was found to greatly affect Pb concentration and isotopic composition: petrol emission-derived particles become dominant immediately following a rain episode following mixing-in of soil-derived particles as the aerosol matures. This mixing was affected by wind direction.

In south Wales, carbon and Pb concentration and isotopic compositions data have been used to identify and partly characterise distinct source areas. Factor analysis indicated that there were four main factors influencing carbon and Pb at these sites: marine, soil, industrial and vehicle emissions. Weather conditions, primarily wind direction, have been associated with the isotopic composition of individual sites. Some of the samples were found to represent mixing of two sources, vehicle exhaust emission derived particles and with seawater-derived particles for example, Broadhaven aerosols.

Therefore, the carbon and Pb parameters used in this study have been relatively successful in identifying sources and characterising source areas. These sources in Wales and Milton Keynes have been found to be greatly influenced by both rain and wind direction.

Chapter 4

The identification of aerosol sources in Milton Keynes using Major and Trace elements

4.0 Introduction

In order to establish the main sources of aerosols and identify weather relationships in the Milton Keynes area, enrichment factors were calculated and a factor analysis of data was conducted. Several trace elements were chosen to be investigated, and the principal parameters used to identify these elements were:

(1) Toxicity in the environment.

(2) Ease of analysis.

These criteria led us to select the following elements (Table 4.0):

aluminium (Al), arsenic (As), barium (Ba), carbon (C), chromium (Cr), cobalt (Co), copper (Cu), magnesium (Mg), manganese (Mn), lead (Pb), antimony (Sb), vanadium (V) and zinc (Zn).

4.1 Sources

From the trace elements chosen for this study, the masses of Al, Co, Cr, Mn, V and their compounds annually transported to the oceans by streams greatly exceed mass transport of these elements through the atmosphere. These elements are lithophiles. In contrast, the elements As, Cu, Pb, Sb, Zn, and their compounds are transported through the atmosphere in significant quantities relative to their transport by streams and are termed atmophiles.

In the past 15 years there has been an increased interest in calculating the emissions of trace elements (Nriagu, 1979; Walsh *et al.*, 1979; Parcyna, 1980; Parcyna, 1983b; Nriagu and Davidson, 1986; Yaaquari *et al.*, 1990; Sigurdsson and Laj, 1992). Section 1.4 in Chapter 1 has detailed information on both the natural and anthropogenic sources of the trace elements in this study. A brief summary of the main sources of trace elements are given below.

Table 4.0

Trace elements in the environment, their main sources and toxicity.

Element	Main Sources	Toxicity
Al	Crustal Building construction	Neurological effects (Alzheimer's decease)
As	Coal combustion	Tumour inducing
Ba	Paints	Poisonous
C	Fossil Fuel Combustion	Tumour inducing
Cr	Vehicles Cr plating Fe and steel industries	Tumour inducing
Co	Coal combustion	Inhibits metabolism
Cu	Smelters Vehicles	Pulmonary toxicity
Mg	Crustal Non-ferrous metal production	Toxic in large quantities
Mn	Non-ferrous metal production	Pulmonary toxicity
Pb	Vehicle exhaust	Biochemical effects on kidneys, testes, bones and the nervous system
Sb	Vehicles Oils and greases	Toxic
V	Oil combustion	Pulmonary and metabolic toxicity
Ni	Oil combustion	Pulmonary and metabolic toxicity
Zn	vehicles; Tyre wear and galvanised chips	Pulmonary toxicity

4.1.1 Soil

Crustal weathering is a major source of trace elements in the environment. Dry deserts are large net contributors of trace elements into the atmosphere. For example Saharan dusts have been found to be transported large distances: for example, Schuetz *et al.* (1981) reported the presence of Saharan dust in North Atlantic samples. Such atmospheric

particles are a result of weathering. Weathering is in turn dependent upon many factors including temperature, rock type and structure, vegetative cover and the elements released by weathering will be dependent upon the weathering material. The elements Al, Fe, Mg, Mn, Pb and Zn, have major crustal erosion sources. In fact Al or Fe are used as references in enrichment factor calculations.

4.1.2 Volcanoes

Volcanoes are estimated to produce between 12 x 10^6 and 150 x 10^6 metric tons of fine particles (radius <20 μm) per year (SMIC, 1970). This is 1 to 20% of the total natural aerosol production rate. However, no exact emission rates for elements such as As, Cd and Zn exist. In fact, there are large discrepancies in the literature. For example, Zoller (1983) indicated that metal fluxes into the atmosphere from individual volcanoes can vary by more than two orders of magnitude. During an eruption, volatile elements evaporate and condense onto particles, which are then transported and subsequently deposited. The main elements which are erupted in this manner are As, Cd, Cu, Hg, Mn, Ni, Pb, Se and Zn. Generally, volcanic emissions are the major natural sources of trace elements in the atmosphere (Table 4.1), although the natural emissions for all but Mn are dwarfed by anthropogenic emissions.

Table 4.1

Volcanic fluxes to the atmosphere compared with anthropogenic and biogenic sources (Sigurdsson and Laj, 1992).

Trace elements	Volcanic ($x10^6 Kgyr^{-1}$)	Anthropogenic ($x10^6 Kgyr^{-1}$)	Biogenic ($x10^6 Kgyr^{-1}$)
Cu	10	35	3
Mn	45	38	30
Pb	4	332	2
Zn	10	135	8

4.1.3 Marine

The oceans cover some 71% of the Earth's surface. Air-sea interaction is thus extremely important in the biosphere. Below 0.2 m of the ocean surface, salt concentrations are high,

but they decrease rapidly within the first metre. This is the layer of direct influence of the large jet drops, most of which rise <0.2 m and return directly to the sea. Figure 4.0 indicates that a few of these giant drops may be carried by turbulence to heights of below a metre before falling back to the sea. From this base level to the cloud base at 600 to 800 m (a sub-cloud layer), the air is well mixed and the lapse rate (excluding adiabatic) becomes more stable. The cloud layer lies above 800 to 2,000 m, with the temperature lapse rate stable. Here, there is a rapid decrease of salt which become negligible at the temperature inversion. The temperature inversion is caused by the fine mist-like drizzle (Woodcock, 1972) which contains salt and do not remain directly beneath the clouds. This is because wind shear causes the clouds to move faster than the sub-cloud air producing a salt inversion. This is coupled with the accumulation zone where high concentrations of salt are carried, the parcels of air grow rapidly as they rise to more humid regions (Woodcock *et al.*, 1963). Some of these particles attain sufficient fall speeds to produce an accumulation or concentration of salt.

These two factors combine to produce the salt inversion layer. The amount of sea salt cycled through the atmosphere is in the order of 10^9 to 10^{10} tons yr^{-1} (Eriksson, 1959, 1960; Blanchard, 1963; Petrenchuk, 1980) with a residence time of days (Blanchard, 1982).

As stated in Chapter 1, bursting of bubbles produced at sea are the major contributors of the marine aerosol. A drop of seawater that enters the atmosphere commonly has a composition close to that of seawater (approximately 3.5% sea salt by weight, 85% of which is sodium chloride). The drop generally begins to evaporate because the relative humidity of the atmosphere lower than the relative humidity over the seawater surface (98%). The salt concentration increases until the drop's vapour pressure is that of the environment, when evaporation ceases. At this stage the drop is a brine drop (Blanchard, 1982).

If the relative humidity of the atmosphere is <70 to 74% the drop becomes supersaturated with sea salt and a sea salt particle is produced (Twomey, 1953).

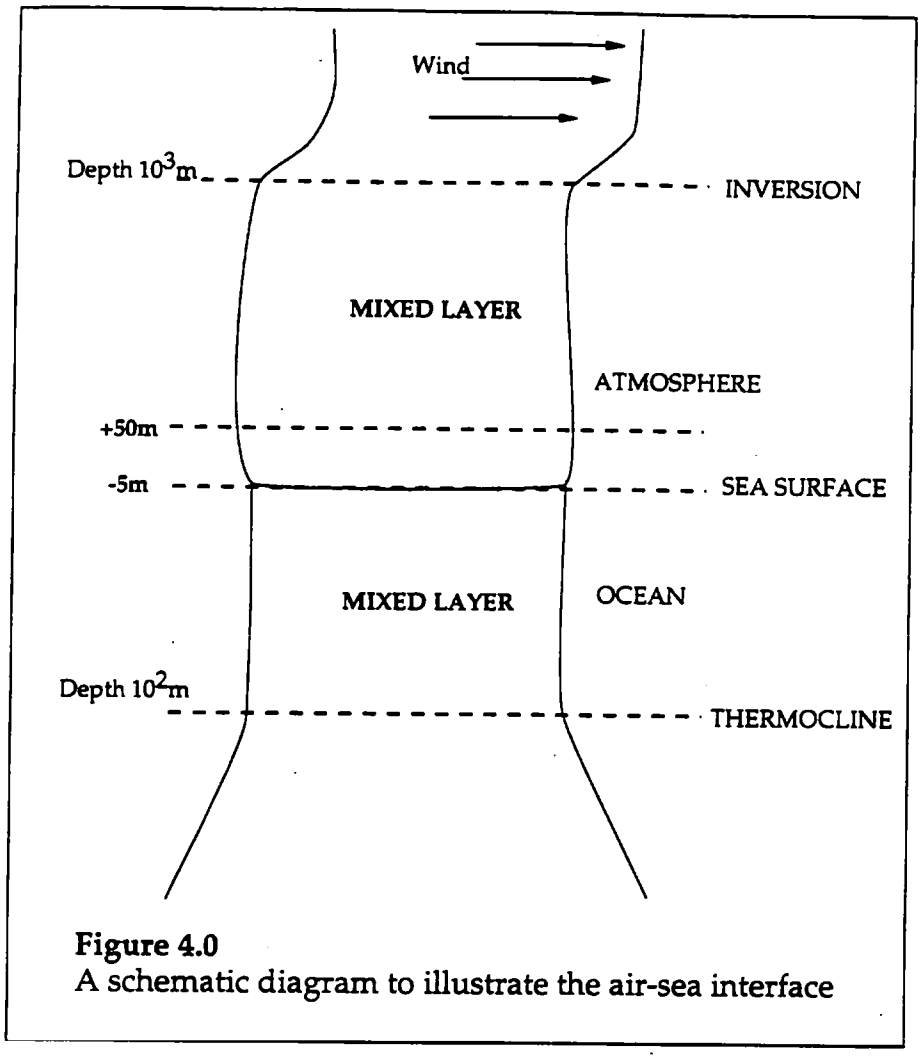

Figure 4.0
A schematic diagram to illustrate the air-sea interface

The present ionic composition of seawater results from a balance between the rate at which dissolved matter is added to the ocean from the land and the atmosphere, and the rate at which it is removed from the sea by incorporation into the atmosphere. Materials enter the ocean either by fall-out from the atmosphere or the influx of river water. Since the concentration of the various elements in seawater approximates a steady state, the rates at which they are supplied to the ocean are balanced by the rate at which they are removed. Barth in 1952 introduced the concept of residence time of an element (T), which is the average time it remains in the sea before being removed:

$$T = \frac{A}{dA/dt}$$

Where,

A = total amount of the element dissolved or in suspension in the ocean.

$\frac{dA}{dt}$ = rate element is added or precipitated.

This method of calculating residence times is dependent upon the estimation of $\frac{dA}{dt}$ .Two methods are used: (i) Barth (1952) used data on the average composition of river water and total amount of river water delivered into the sea annually to estimate rate. It is necessary to further estimate the transfer of elements to the sea via the atmosphere and precipitation to the rivers. (ii) Goldberg and Arrhenius (1958) suggested that data on the median rate of marine sedimentation and the average composition of marine sediments produced a more accurate estimation of rates. There is surprisingly good agreement between both methods. For example, the residence time of Pb in marine waters has been estimated at 400 yrs (Goldberg, 1971). This value represents its involvement in biological reactions and its uptake by marine organisms. However, Pb residence time alters dramatically to a month in highly productive coastal waters (Bruland *et al.*, 1974). This strongly emphasises the biological interactions of Pb. Table 4.2 lists the concentrations of various elements within the Earth's crust and ocean water residence times.

Table 4.2

The concentration of elements in the Earth's crust and oceanic water, with estimated residence times in oceanic water (Goldberg, 1971).

**na = no data available.*

Element	Earth's crust ($mg\ g^{-1}$)	Ocean water ($mg\ g^{-1}$ s= 35%)	Oceanic residence time
Al	8.2×10^{4}	5	100
As	1.8	2.3	n.a*
C (Inorganic)	Extremely variable	4.5×10^{3}	150
Co	25	0.08	1.8×10^{4}
Cr	100	0.6	350
Cu	55	3	5×10^{4}
Mg	2×10^{4}	1.32×10^{6}	4.5×10^{7}
Mn	950	2	1,400
Pb	12.5	3×10^{-2}	400
Sb	0.2	0.2	3.5×10^{5}
Zn	70	5	1.8×10^{5}

Residence time is also influenced by particle size. Blanchard and Woodcock in 1980 stated that the number of particles of >2 μm radius increases from 3×10^{5} m^{-3} to 7.5×10^{5} m^{-3} with a corresponding wind speed increase of 4.4 to 15.5 ms^{-1}. However, for particles of >40 μm radius, the increase in concentration is from 0.1 to >100 m^{-3}. This is thought to represent the shorter residence time of the large particles which respond more quickly to the changes in wind speed. Consequently, large particles are more likely to be in equilibrium with the wind speed than small particles. The small particles thus have a long residence time and a sluggish response to changes in wind speed (Blanchard, 1963; Toba and Chaen, 1973); for example sea salt particles of 0.3 μm radius show little response to changes in wind speed while particles of 15 to 17 μm radius respond rapidly. These particles become directly proportional to the source of particles, the area covered by whitecaps (Monahan *et al.*, 1982). This lack of response to wind speed by sub-micron particles influenced the choice of the particle size sampled in this study. The 0.5 to 5 μm size range was chosen because it represents particles which are little affected by wind speed, reducing the wind variables to wind direction alone.

4.1.4 Anthropogenic Emissions

Vehicular traffic, energy generation and industrial metal production have produced an increase in trace element emissions into the environment. Murozumi *et al.* (1969) reported that within the ice and snow of the Greenland ice sheet an increase in Cd, Cu, Pb and Zn concentration had been recorded from the 1820's (start of industrial revolution in Europe). Heron *et al.* (1977) identified early atempts of Zn smelting in the 1100s and the surge in Zn emissions in the 1970s (Figure 4.1). This increase in concentration was paralleled by the increase in European coal production (Erlenkeuser *et al.*, 1974). Coal combustion is chiefly responsible for emitting Be, Co, Mo, Sb and Se (Table 4.0) while oil firing releases Ni and V. Non-ferrous metal releases As, Cd, Cu and Zn, with Fe and steel production releasing Cr and Mn. Lead is primarily introduced into the recent environment by petrol combustion (Table 4.0). However, there are other high temperature processes such as smelting which may introduce Pb into the environment.

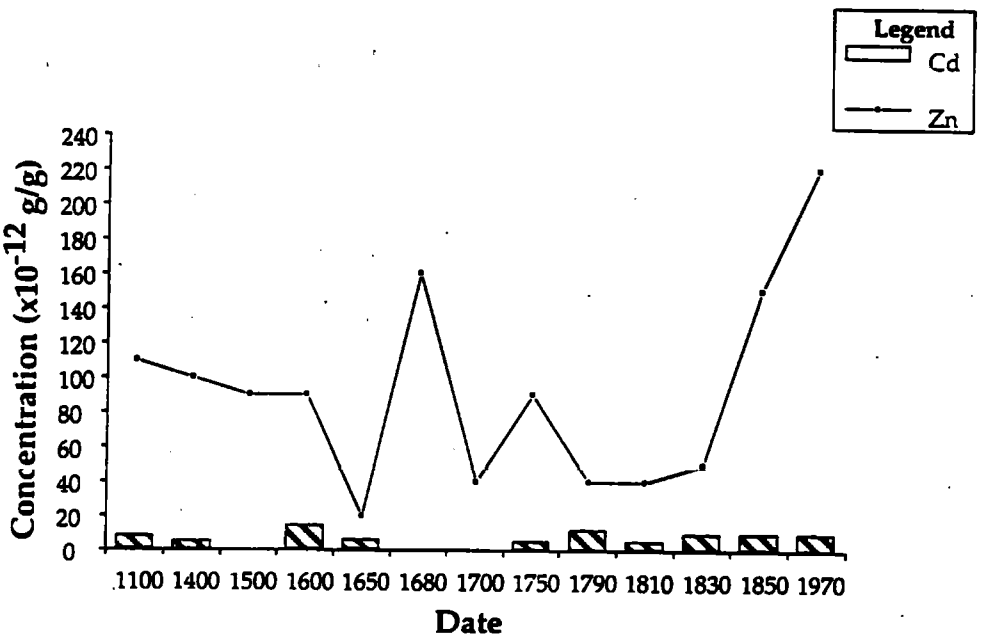

Figure 4.1
Milcent, Greenland: variations of Cd and Zn concentration as a function of time (Henon *et al*, 1977).

The mobilisation of certain heavy metals to the ocean via the atmosphere is induced mainly by three high-temperature industrial processes: the combustion of fossil fuels, metal smelting and the production of cement. Bertine and Goldberg (1971) estimated fluxes of heavy metals due to fossil fuel burning by utilising the consumption of fossil fuels in 1961: coal 1.75×10^{5} g; lignite 1.04×10^{15} g; fuel oil 1.63×10^{5} g and natural gas 0.66×10^{15} g. Today these figures would be higher. For Ba and Co, fossil fuel mobilisation to the atmosphere appears to be similar to river fluxes to the oceans. However, As, Cd, Sn, Pb and Zn are more easily volitalized and thus introduced into the atmosphere at higher concentrations.

Smaller particles are emitted into the atmosphere by cement production. In 1972 the EPA estimated that particulate emissions from cement manufacturing was 860,000 tons yr^{-1}

(during cement production). The elements As, B, Pb and Zn are mobilised into the atmosphere at greater concentration in cement manufacture than during fossil fuel combustion.

Two case studies, the Antarctic and Arctic, were chosen to illustrate both the influence of trace elements in the atmosphere and the dominant research interest during the last decade.

Antarctica

The natural sources of trace elements in the Antarctica atmosphere are wind-blown crustal dust, sea-spray and volcanism. Data from Antarctic ice cores indicate that during pre-industrial times the total Pb content of snow was $\frac{2}{3}$ accounted for by crustal contribution and $\frac{1}{3}$ by volcanism with marine contributions being negligible (Boutron and Patterson 1987). More recently, higher concentrations of Pb have been found in Antarctic snows which can not be accounted for by these natural sources alone and anthropogenic sources have been suggested (Wolff and Peel, 1985; Dick, 1987; Boutron & Patterson, 1986). The increased concentrations in Zn, Cd and Cu have been identified as having anthropogenic sources.

Arctic

Soot, sulphur and trace elements have all been found in Arctic aerosols. The Arctic winter aerosol may be responsible for the formation of the Arctic haze and may affect the atmospheric budget and the acidity of precipitation (Nriagu & Davidson, 1986). The origin of the aerosol is thought to be from mid-latitude regions by long-range atmospheric transport. The "Arctic haze" is thought to occur in winter because of reduced precipitation in the Arctic which allows the accumulation of trace elements and thus increases the normal atmospheric residence time (Rahn & Macaffrey, 1980; Rahn, 1981a; Carlson, 1981). Rahn (1977) identified the position of the polar front as being responsible for the winter enhancement of trace elements. The polar front is a zone of intensive mixing between temperate and polar air masses; the mixing processes in the Iceland and Atlantic lows developing at the polar front, are accompanied by strong precipitation and produce heavy

scavenging. Thus, the polar front acts as a barrier to meridional mixing and aerosol transport (Winkler, 1983). In the winter, the polar front lies south of populated and industrialised areas. In summer, the Arctic atmosphere is isolated from lower latitudes by the polar front in its northern position and the atmosphere circulation is confined to the Arctic. Therefore, the Arctic atmosphere behaves as a reservoir that becomes progressively 'dirtier' throughout the winter and is "cleaned" during the summer.

4.1.5 Trace elements and particle size distribution

The size distribution of atmospheric particles can be expressed as a surface or mass-density function. Whitby (1975) calculated a trimodal size distribution function for typical urban aerosols (Figure 4.2). This trimodal distribution consists of a nucleation, accumulation and coarse mode. Particles are formed during high energy combustion and from gas to particle conversion reactions. The nucleation mode consists of particles of 0.005 to 0.1 μm aerodynamic diameter (AD) consisting of ions. The accumulation mode particles have a size range of 0.1 to 2.5 μm AD and originate from coagulation and condensation processes between the ion nucleation mode particles (McMurry & Wilson, 1982 & 1983). The coarse mode particles range from 2.5 to 100 μm AD and are formed by mechanical processes, for example erosion and combustion of ash-containing fuels. Various cascade impactor studies have identified that trace elements are concentrated into size. Davidson and Osborn (1986) reported that Cd, Pb and Zn are predominantly found in the accumulation mode (0.3 to 0.8 μm), Al, Ca and Mg in the coarse mode (AD >3 μm) and Ca, Cr, Mn and V are intermediate (AD 1 to 5 μm). This distribution is thought to reflect the generation of the trace element particles.

4.2 Sample collection and analysis

Sample collection was conducted at the Milton Keynes site. The same collection technique for Pb (1 M HBr) was used to collect the trace element samples (Chapter 2). Samples were stored at room temperature and in the dark (to reduce the deterioration of HBr by U/V

radiation). The analysis of samples consisted of the direct nebulisation of the solution into the ICP-MS (Chapter 2). No sampling efficency for trace elements was undertaken.

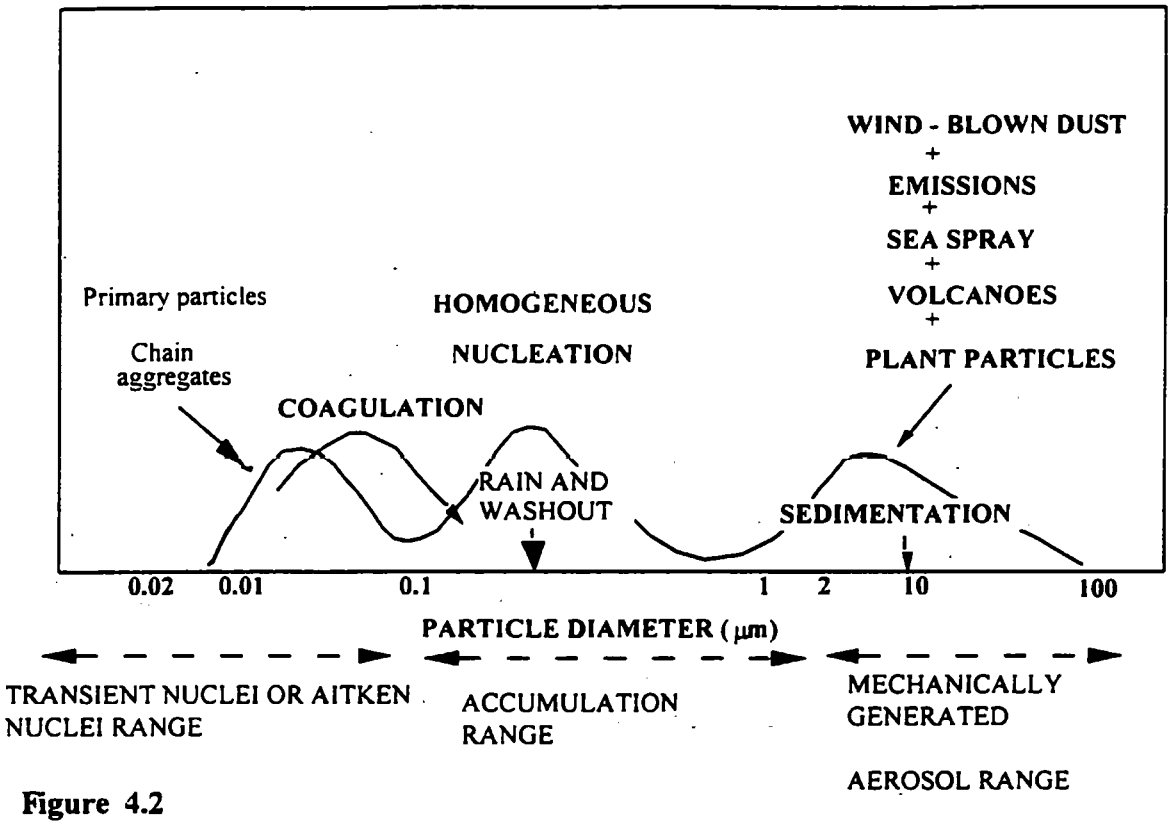

Figure 4.2

Atmospheric aerosol distribution showing the principal modes, main sources of mass for each mode, and the principal process involved in inserting mass in each mode, (Whitby *et al*,1975).

4.3 Description of trace element variation.

The concentration values of the trace elements for the Milton Keynes site vary from a maximum Al concentration of 76.51 ng ml^{-1} (3/7/92) to a minimum concentration of 0.2 ng ml^{-1} of As (17/7/92) Appendix B(i). These concentrations are similar to measurements by Yaaquari *et al.* (1990) in East Anglia, UK. Several groupings of elements have been identified by simple minimum and maximum observation and correlation coefficients. These groupings exhibit similar trends in concentration with time and correlate strongly with each member in the group (Figures 4.3 and 4.4).

Group 1.

This grouping of elements consists of Al, Ba, Co, Mg, Pb, Sb, V and Zn. The elements within this group exhibit similar concentration variations throughout the year (Figure 4.3) and strongly correlate with each other (Appendix C(i)). The elements in group 1 can further be sub-divided by strong correlation of those elements which have relatively low concentrations of <25.0 ng ml^{-1} (Ba, Co, Pb, Sb and V) and those with relatively high concentrations of >25.0 ng ml^{-1} (Al, Mg and Zn):

(a) The elements Al, Mg and V exhibit relatively high concentrations of >25.0 ng ml^{-1} and three concentration highs over the period February 1992 to April 1993: (1) 3/7/92, (2) 27/11/92 and (3) 25/4/93. The elements Al, Mg and V all exhibit strong positive correlations with the each other and other group 1 elements: for example Mg correlates with Al ($r = 0.65$, $p < 0.0001$), Ba ($r = 0.56$, $p =< 0.0001$), and Sb ($r = 0.97$, $p =< 0.0001$). These elements have been termed Group 1A. The variation in concentration of these elements with time indicates that on these days external variables, such as wind direction and rain, exerted influence on the concentration of these elements.

(b) The Group 1 elements Ba, Co, Pb, Sb and Zn exhibit relatively low concentrations of <25.0 ng ml^{-1} and seven concentration highs over the period February 1992 to April 1993: (1) 3/7/92, (2) 9/10/94, (3) 22/11/94, (4) 27/11/92, (5) 15/12/94, (6) 25/4/93 and (7) 25/4/93. These elements all exhibit strong positive correlations with each other and other group 1 elements, for example Pb exhibits positive correlations with Co ($r = 0.61$, $p =< 0.0001$) and Ba ($r = 0.75$, $p =< 0.0001$).

The element Co exhibits greater constancy with time than any other measured element. There are relatively long periods of stability for example, 19/5/92 to 22/6/92 and 17/7/92 to 16/9/92. The element Zn exhibits weak negative correlations with all group 1 elements. This negative relationship with Group 1 elements indicates that an inverse relationship exists.

Figure 4.3
Group 1 element variation of concentration with time. The 3 dimensional diagram identifies 4 main concentration peaks exhibited by the group 1 elements (Al, Ba, Co, Mg, Pb, Sb, V and Zn) .

Group 2

The data for Cr, Cu, Mn and Ni are scant mainly due to analytical difficulties (Appendix C(i)). However from this limited dataset it was still possible to identify concentration trends within these elements with time (Figure 4.4).

(a) Chromium; Cr and Ni exhibit concentration peaks on the (1) 8/9/92 (2) 23/10/92 and (3) 26/11/92. Cr exhibits strong positive correlations with the group 2 element Mn ($r = 0.90$, $p =<0.0001$). Cr, Mn and Ni exhibit strong positive correlations with each other, for example Cr exhibits positive correlations with Ni ($r = 0.5$, $p =<0.0001$) and Mn ($r = 0.90$, $p =<0.0001$).

(b) Copper exhibits a varied concentration with a mean of 5.4 ng ml^{-1}. The two main concentration peaks are identifiable; (1) 29/7/92 and (2) 15/9/92. Cu exhibits no appreciable correlations ($r < 0.1$, $p =<0.0001$) with the other group 2 elements. In fact, Cu does not exhibit strong correlations ($r < 0.5$, $p =<0.0001$) with any of the trace elements in this study. The concentration of elements within this group exhibit maximum and minimum concentrations on different days to that of group 1 elements. This group of elements may reflect the relationship between element concentration and weather conditions, such as wind direction. However, the fact that there are 2 groups of elements indicates that there is another factor influencing element abundance. This factor is thought to be related to the source of the elements and the 2 groups indicate at least 2 discrete sources. Therefore in order to refine the source identification, normalisation calculations and enrichment factors were calculated to assess natural source contributions, such as the crustal/soil contribution.

Figure 4.4
Group 2 element variation of concentration with time. The 3 dimensional diagram identifies 4 main concentration peaks exhibited by the group 1 elements, (Cr, Cu, Mn and Ni) .

4.3.1 Identification of trace element sources

Group 1 elements were divided into 2 sub-groups:

(a) Group 1A.

High concentration (>25.0 ng ml^{-1}) group 1 elements Al, Mg and V all exhibit strong correlations with one another ($r > 0.7$) indicating their similar behaviour. The element Al is a good indicator element and was thus chosen as a representative element for this sub-group.

(b) Group 1B.

Low concentration (<25.0 ng ml^{-1}) group 1 elements Ba, Co, Pb, Sb and Zn all exhibit strong correlations ($r > 0.5$) with one another indicating their similar behaviour. For clarity and simplicity, Pb was chosen as a representative element because it can be related to the Chapter 3 data.

In order to identify possible trends the dataset was first normalised to Al to remove the influence of any crustal component and also to Pb which has been taken to indicate anthropogenic influence. Mean seawater and crust trace element data were taken from Taylor and McLennan (1981) with refuse and power generation data from Nriagu and Davidson (1986).

Thus mean crustal, seawater, refuse and power generation ratios were used to identify possible aerosol components. It must be emphasised that these mean values may contain large errors. For example the mean power generation trace element values will vary with ore and plant operating conditions. However, little data are available overall and thus this exercise is a preliminary assessment of the dataset, which is later validated by statistical analysis.

The Group 1 elements Ba, Mg, Sb, and Zn when normalised to Al indicate 4 components representing a seawater component with 3 unknown components A, B and C (Figure 4.5). The identified component for Ba, Co and Zn was crustal with Sb exhibiting a seawater

One of the 3 unknown components A, B and C may represent vehicle influence with components B and C resulting by mixing seawater and component A. The elements Pb and V are however, not explained by crustal and seawater components (Figure 4.6). This is thought to indicate a mainly anthropogenic origin of Pb and V. Thus, in order to assess the vehicle component the dataset was also normalised to Pb.

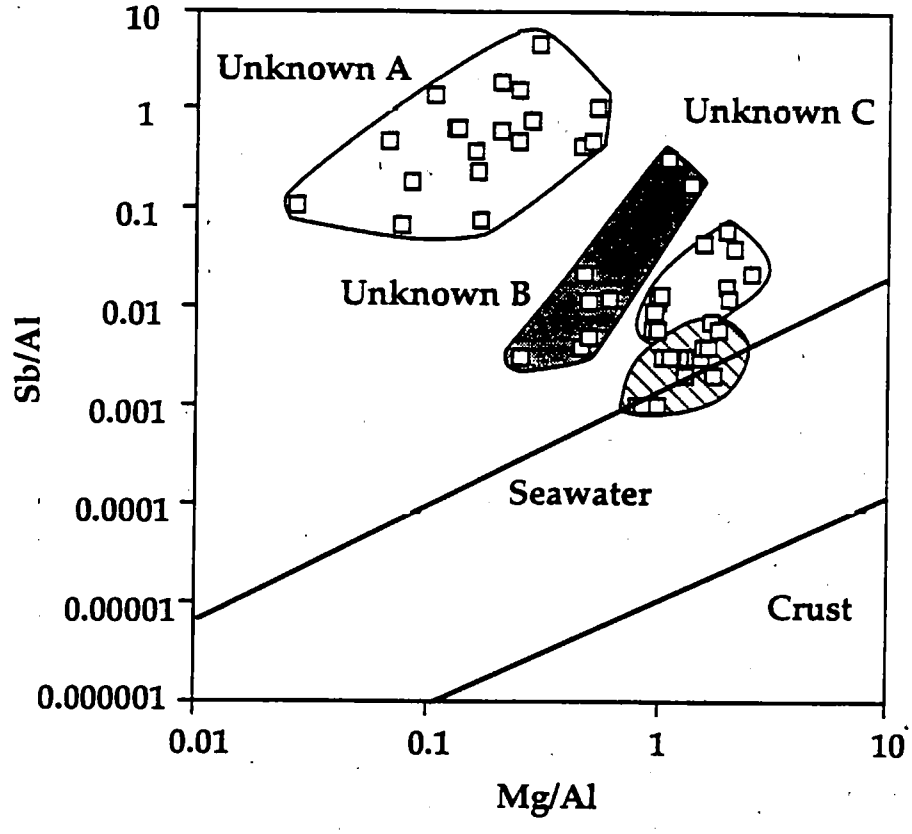

Figure 4.5
Group 1 elements (Sb, Mg, Zn, Ba and Co) when normalised to Al exhibit 3 unknown components, A, B and C, with a seawater (Sb) or a crustal (Ba, Sb and Zn) component . The unknown components are thought to represent anthropogenic components, possibly vehicle derived.

The Group 1 elements component means and standard deviations have been tabulated (Table 4.3). The elements Ba, Co, Mg, Sb and Zn when normalised to Al resulted in distint component groups: A, C and seawater populations.

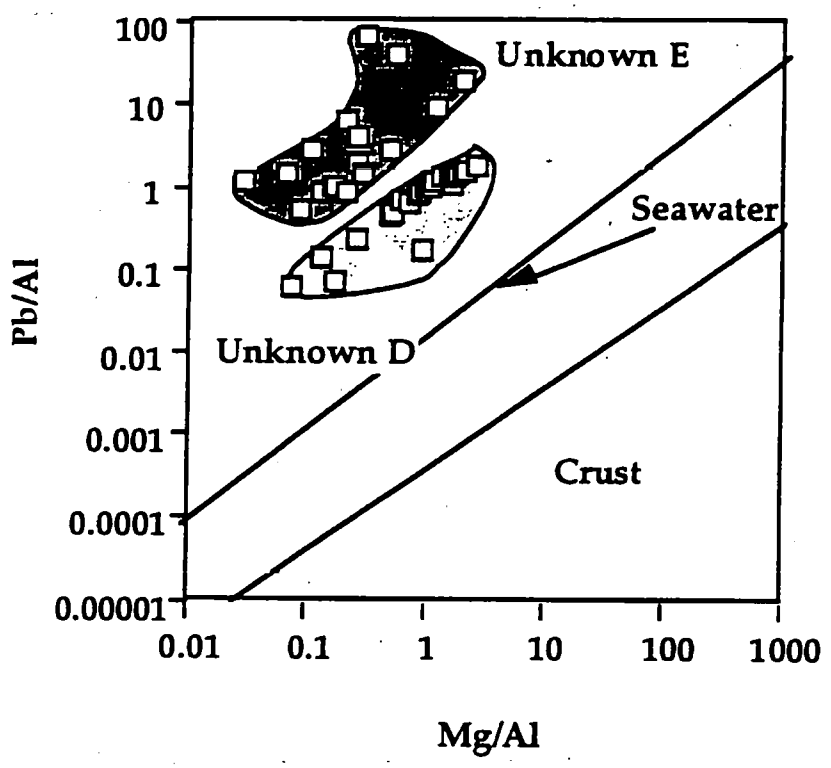

Figure 4.6
Pb when normalised to Al exhibits 2 unknown components, D and E, with no seawater or crustal components . The unknown components are thought to be vehicle derived anthropogenic components.

Table 4.3

The mean and standard deviation of normalised components (to Pb and Al).

Element ratio	Mean EF values	Standard deviation (1σ)
Co/Pb *Crust*	0.46	-
Seawater	0.01	-
Power Gen.	0.67	-
Refuse	0.14	-
H	0.008	0.03
Cr/Pb *H*	0.11	0.069
I	0.01	0.003
J	0.01	0.002
Crust	0.03	0.011
Seawater	3.0	-
Power Gen.	0.11	-
Refuse	0.14	-
Ni/Pb *Crust*	0.004	0.0001
Seawater	1.5	2.58
Refuse	0.14	-
V/Pb *Crust*	3.1	-
Seawater	3.3	-
H	0.1	0.069
Refuse	0.3	-
Zn/Pb*Crust*	0.89	-
Seawater	3.0	-
I	0.01	0.003
J	0.01	0.007
Power Gen.	1.1	-
Refuse	104.3	-
Ba/Al *A*	1.4	0.24
B	0.3	0.02
C	0.01	0.001
Seawater	0.01	-
Crust	1.2	-
Co/Al *A*	0.1	0.04
B	0.02	0.01
C	0.01	0.001
Seawater	0.002	-
Crust	0.001	-
Cr/Al *Crust*	0.003	-
Seawater	0.025	-
H	0.1	0.06
Refuse	0.04	0.05
Cu/Al *F*	1.02	0.32
Crust	0.003	-
Seawater	0.073	-

Table 4.3 (Continued)

The mean and standard deviation of normalised components (to Pb and Al).

Element ratio	Mean EF values	Standard deviation (1σ)
Mg/Al *A*	0.2	0.1
B	0.8	0.2
C	1.3	0.2
D	1.6	0.4
E	0.43	0.4
F	0.63	0.4
G	1.4	0.5
Crust	0.44	-
Seawater	0.01	-
Mn/Al *G*	0.002	0.001
Crust	0.1	-
Seawater	0.02	-
Pb/Al *E*	0.6	0.3
D	5.5	1.31
Seawater	0.01	-
Crust	0.33	-
Sb/Al *A*	0.9	1.0
B	0.03	0.02
C	0.01	0.001
Seawater	0.003	-
Crust	0.001	-
V/Al crust	5.43	-
Seawater	0.01	-
Zn/Al *A*	2.0	0.41
B	0.04	0.02
C	0.01	0.001
Seawater	0.01	-
Crust	0.004	-

When Pb was normalised to Al, two unknown components D and E were not identified with seawater or crustal influences (Figure 4.6). The mean and standard deviation of the unknown components D and E have been tabulated (Table 4.3).

The group 2 elements, Cu and Cr when normalised to Al indicate 2 components, seawater and an unknown F, which may represent vehicle-derived particles (Figure 4.7). However, the group 2 elements Mn and Ni do not exhibit these trends. The element Mn exhibits three components, crust, seawater and an unknown G, which may represent vehicle derived particles (Figure 4.8). Ni does not exhibit a crustal or seawater component. The mean and standard deviation of the unknown components F and G have been tabulated (Table 4.3).

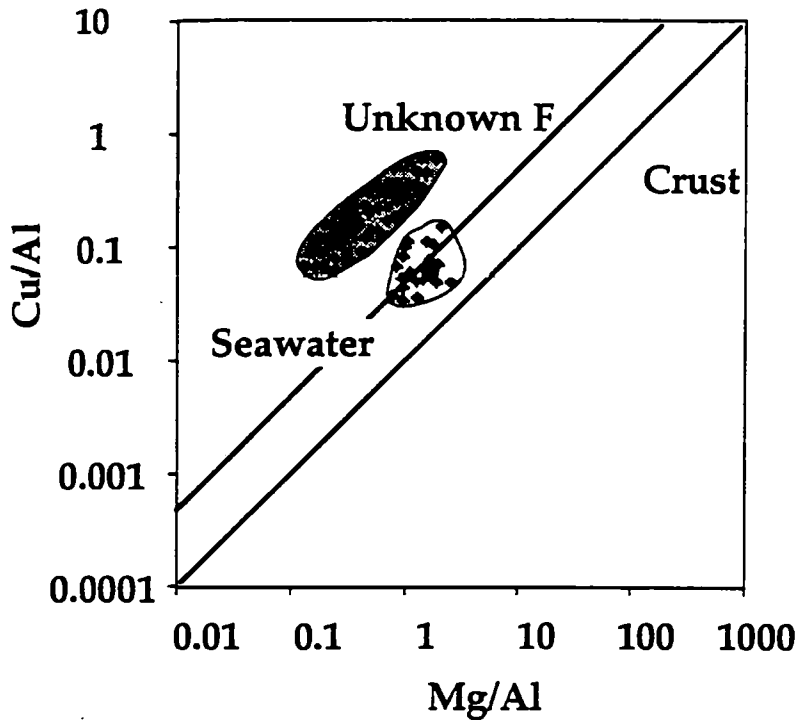

Figure 4.7
Normalising to Al indicates that Cu exhibits 2 components, seawater and an unknown, which is thought to be vehicle derived.

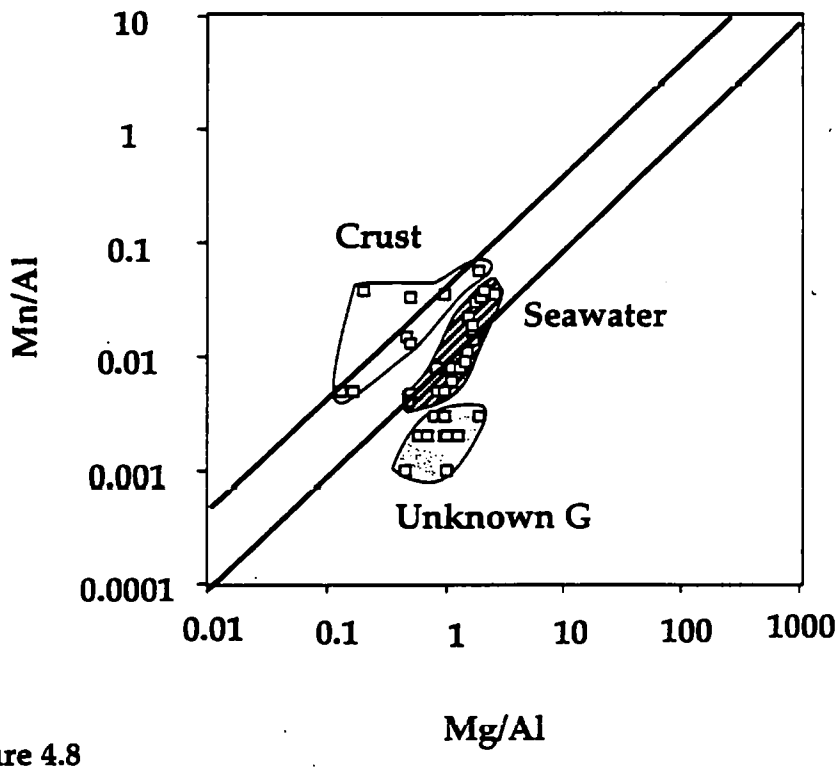

Figure 4.8
Mn was found to exibit 3 components, seawater, crust and an unknown component G, possibly vehicle derived.

The unknown components may represent another factor affecting the data such as wind direction. It is suggested that further data be collected to clarify the origin and classification of these components.

Thus it appears that for groups 1 and 2 there is evidence of both natural and unknown anthropogenic components. In order to assess this anthropogenic component the dataset was normalised to Pb and compared to refuse and power generation trace element ratios.

The elements Cr, V and Co when normalised to Pb exhibit two components thought to represent the combustion trace element ratios of domestic refuse and an unknown component H (Figure 4.9). The unknown component appears not to be influenced by seawater, crustal or power generation components. A refuse component possibly originating from an incinerator, is a possible contributor.

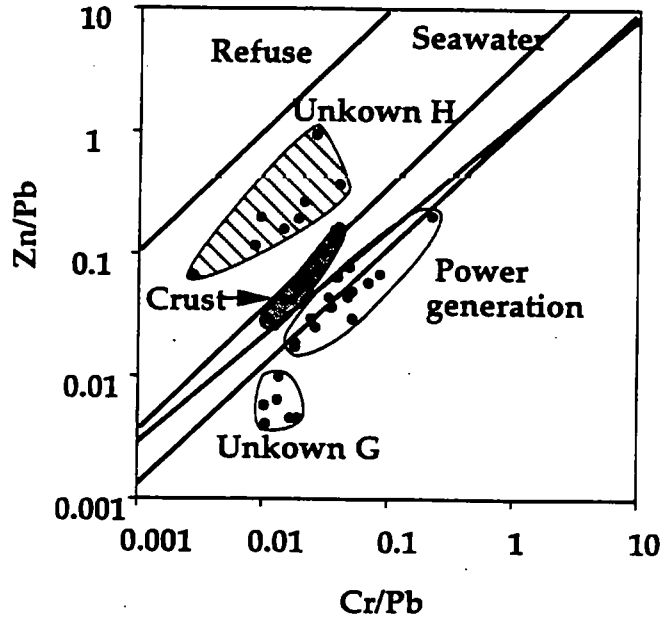

Figure 4.9
Cr and Zn when normalized to Pb produce values which indicate 4 source components, two of which are comprable to power generation and crust trace element ratios. However, there are 2 other components which are unaccounted for, G and H. These may reflect anthropogenic sources, such as vehicles.

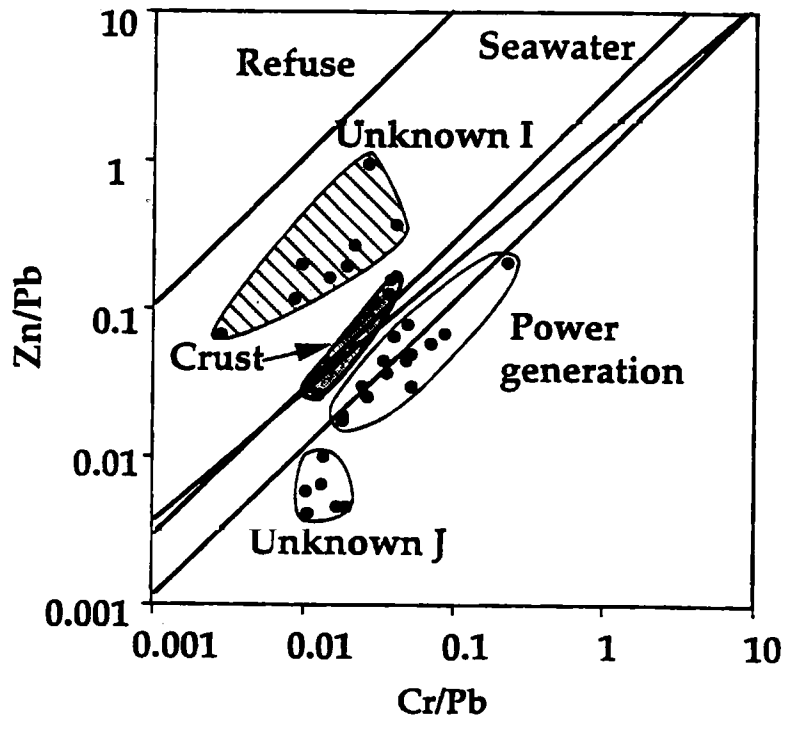

Figure 4.10
Cr and Zn when normalized to Pb produce values which indicate 4 source components, two of which are comparable to power generation and crust trace element ratios. However, there are 2 other components which are unaccounted for. These may reflect anthropogenic sources, such as vehicles.

The mean and standard deviation of the unknown component H has been tabulated (Table 4.3).

In order to remove the influence of vehicles the element populations were normalised to Pb. Zinc was chosen to represent group 1 elements and Cr to represent group 2 elements.

Chromium and Zn when normalised to Pb indicate 4 components; 2 unknown (I and J) crustal and power generation influence (Figure 4.10). This indicates that when the vehicle influence is removed other components become apparent. Thus, power generation, refuse and crustal influence appear to exert a secondary influence which is blanketed by the

primary vehicle signature. The unknown components may reflect vehicle and/or soil influence.

The mean and standard deviation of the components have been tabulated (Table 4.3).

Cr is a group 2 element which correlates with Mn (r = 0.9) and Ni (r = 0.5). Thus Cr was taken to be representative of Mn and Ni. Cu is also a group 2 element but does not correlate well with Cr, Mn and Ni and is thus discussed separately.

When normalised to Cr, Ni and Pb ratios indicate crustal and component (Figure 4.11). Normalised Mn values also exhibited similar values, crustal and power generation and two unknown components. The mean and standard deviation of the components have been tabulated (Table 4.3).

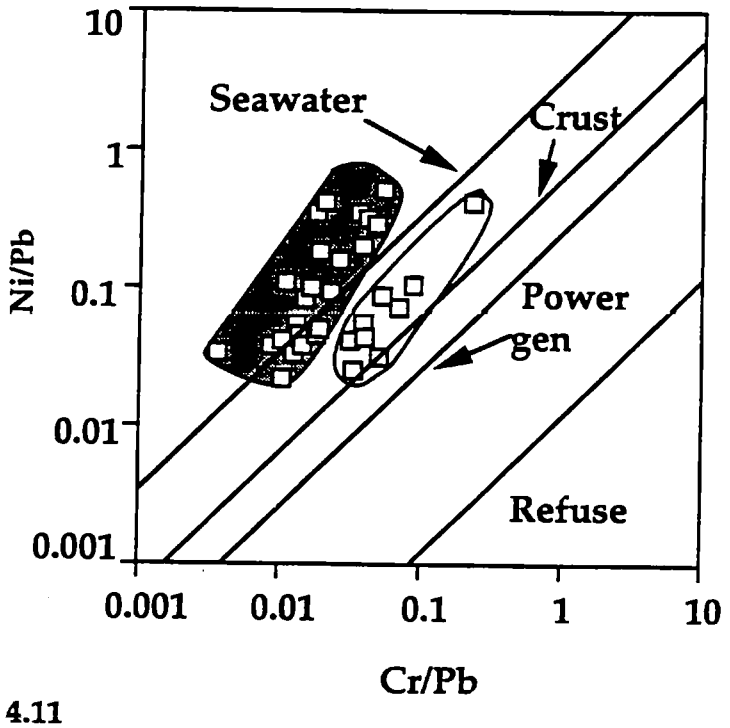

Figure 4.11
Cr and Ni when normalised to Pb produce trace element ratios similar to crustal ratios. This implies that there is a crustal source component.

When Cu was normalised to both Al and Pb one component was apparent, although this component remains unknown.

This preliminary investigation into the source components of trace elements at Milton Keynes indicated that there are several components; seawater, crust, refuse, power generation and several unknowns. The unknown components may reflect vehicle, soil and wind direction influence. These possible sources were further investigated using enrichment factors and factor analysis.

4.4 Rain

Trace elements did not exhibit a relationship with wind direction. However, a relationship with rain was established for the group 1 elements (Figure 4.12). This relationship indicates that group 1 elements are washed out of the atmosphere during a rain episode. Thus, concentration of Al, Ba, Mg, Pb, Sb, V and Zn within the atmosphere decline with rain. This observation compliments the Chapter 3 investigation which also indicated an association between rain and Pb concentration. When normalised to Pb the ratios of Al and V indicate that there is 1 controlling component, which is thought to be rain.

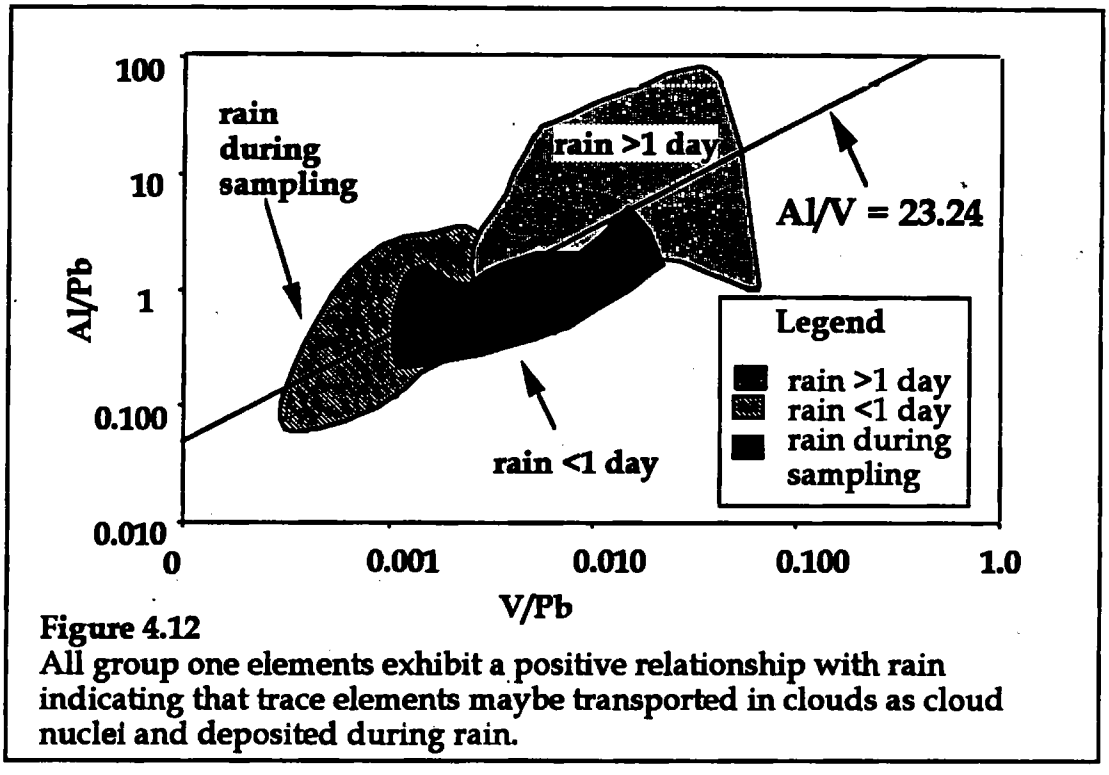

Figure 4.12
All group one elements exhibit a positive relationship with rain indicating that trace elements maybe transported in clouds as cloud nuclei and deposited during rain.

4.5 Enrichment factors

The dataset was subjected to preliminary source identification by calculating enrichment factors, a commonly used method for estimating the source of trace elements within the atmosphere (Zoller *et al.*, 1974; Duce *et al.*, 1975; Nriagu and Davidson, 1986). Simply, the enrichment factor (EF) is the proportion of element X to a reference element in air in relation to its abundance in crust or seawater:

$$EF_{crust} = \frac{X_{air}/Al_{air}}{X_{crust}/Al_{crust}}$$

where

X_{air} and Al_{air} = airborne concentrations of any element X and Al

X_{crust} and Al_{crust} = concentrations of any element X and Al in the crust.

The crustal composition data is taken from Taylor (1964). Values of EF_{crust} near unity suggest that crustal erosion is the primary source of element X; values much greater than unity imply the importance of other sources, such as anthropogenic activities, volcanism and aerosol production at the air-sea interface (Duce *et al.*, 1975). In this study, values of EF_{crust} and $EF_{seawater}$ have been calculated (Al and Mg are the reference elements). Summer (May to August 1992) and winter (September 1992 to April 1993) enrichments have been calculated in order to assess seasonal alterations in elemental source contributions. EF calculations are summarised in Figures 4.13 and 4.14.

Aluminium was chosen as the crustal reference element because it is commonly used as such (Duce *et al.*, 1975 and Nriagu and Davidson. 1986). Both Mg and Na are commonly used as reference elements for seawater EF calculations (Piotrowicz *et al.*, 1979; Weisel, 1981). The elements Ba, Mg, and V exhibit EF_{crust} values which indicate a crustal source (Figure

4.13). However, Pb and Zn both exhibit EF_{crust} values greater than unity in winter, with values close to unity in summer. Conversely, Co and Mn exhibit EF_{crust} values close to unity during the winter months. These seasonal variations may indicate that the source is not constant and is influenced by season. For example, during winter when there is a greater demand for domestic heating there would be a greater output of elements produced by fossil fuels combustion. Seawater or crustal sources do not account for Cr, Cu, Ni and Sb with Mn, Co, Pb and Zn being partially accounted for (Table 4.3). These unaccounted elements are probably anthropogenic in origin. Such large enrichments may results from a variety of natural as well as anthropogenic processes. EF calculations provide little information on sources of such enriched aerosols and to identify the types and locations of aerosol sources, more sophisticated techniques must be employed. Therefore, a factor analysis was preformed to further characterise the sources of trace elements.

EF_{crust} values indicated that BA, Mg and V could be accounted for by crustal sources during both the summer and winter months (Figure 4.13). However, such a relationship was not identified by factor analysis (see below). In fact these elements fall into factor 1 which has been described as the vehicle component. Such conflicting evidence may be the result of potential EF calculation problems:

(1) The variation in crustal composition from one site to another. Use of average compositions, such as those by Taylor (1964) may provide misleading results if the crustal composition near the aerosol sampling site is substantially different from the average composition data used to calculate enrichment.

(2) Although most crustal aerosol is derived from erosion of soil, more complete datasets are available for elemental composition of rock and hence the latter reference material is generally used. Rahn (1976) reported that the chemical composition of crustal aerosol resembles a combination of characteristics of both rock and soil, implying that soil composition data might not be the obvious choice even where more complete soil data is available.

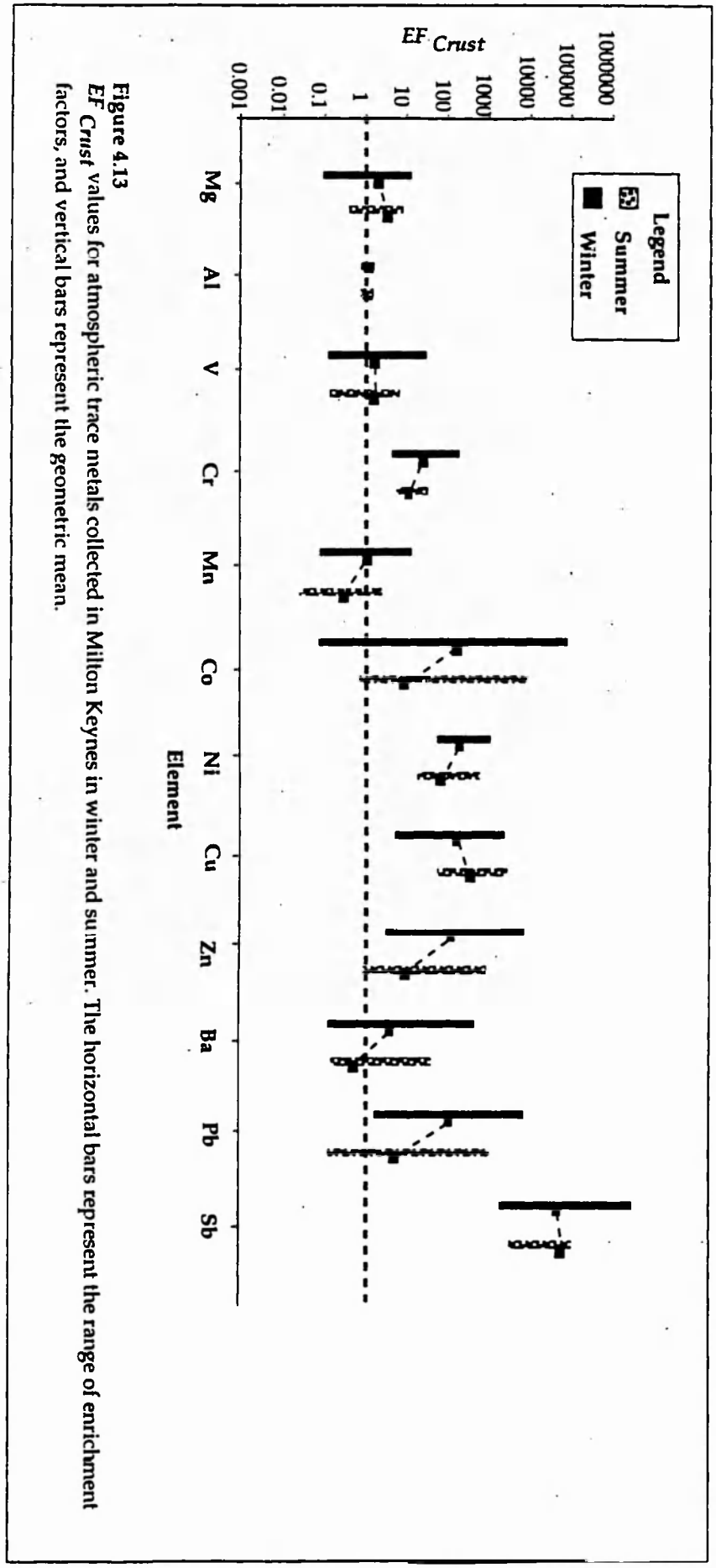

Figure 4.13
EF Crust values for atmospheric trace metals collected in Milton Keynes in winter and summer. The horizontal bars represent the range of enrichment factors, and vertical bars represent the geometric mean.

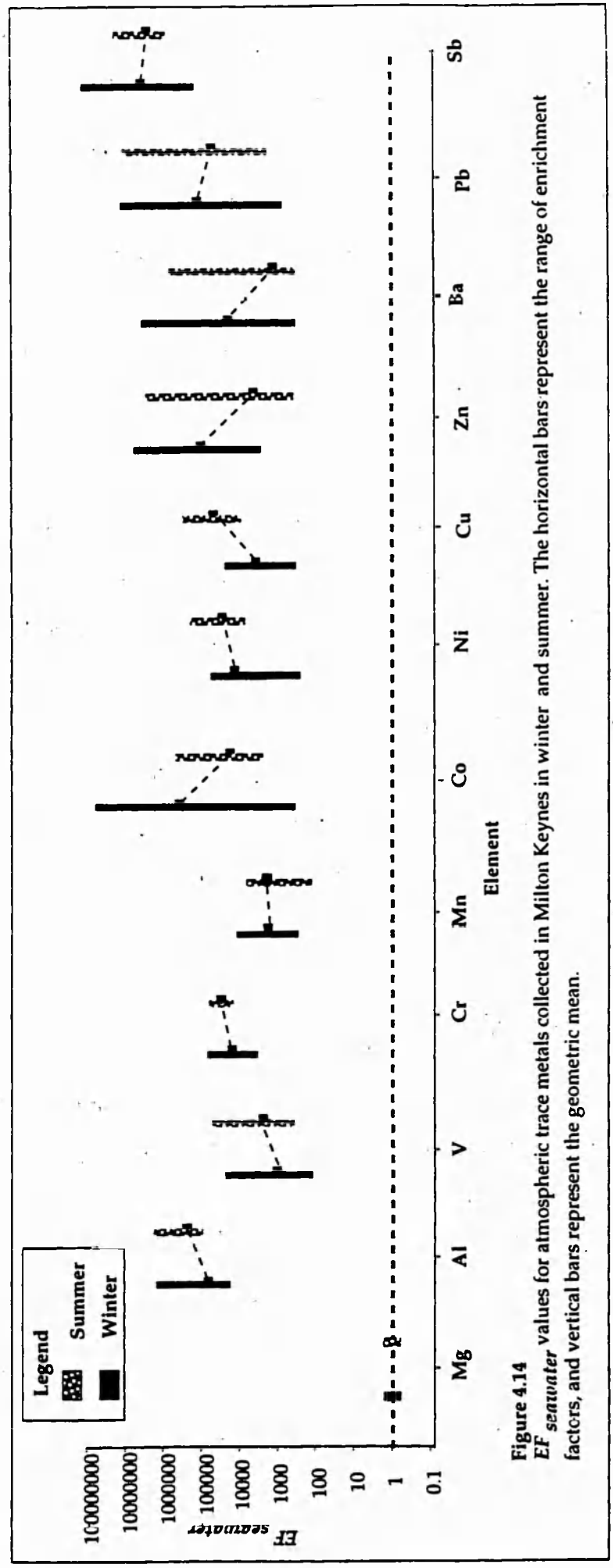

Figure 4.14
$EF_{seawater}$ values for atmospheric trace metals collected in Milton Keynes in winter and summer. The horizontal bars represent the range of enrichment factors, and vertical bars represent the geometric mean.

(3) Physical fractionation (difference in the size distributions of aerosols compared with that of the parent material) has been found to influence aerosol composition. For example, Schuetz and Jaenicke (1974) demonstrated that crustal aerosols found several metres above the ground are derived preferentially from the smallest particles present in the soil. This fractionation coupled with the fact that the chemical composition of most soils varies with particle size, indicates that the elemental composition of the aerosol may be different from the bulk soil (Miller *et al.*, 1972).

Thus, EF calculations are flawed and may only hint at the possible sources of aerosol elemental composition. EF calculations were thus used as a crude and prelimanary examination of a large dataset. Nevertheless, in this study EF calculations did in fact suggest were crustal in origin. EF values also identified Ba, Co, Mg, Mn, Pb, V and Zn as having a crustal source. Although EF calculations exhibit limitations with respect to the interpretation of sources, a preliminary investigation did produce a link with crustal sources. Analysis of trace element data required more than a general data analysis technique; a more specific statistical analysis tool (factor analysis) was implemented in identifying sources and weather relationships.

4.6 Statistical Analysis

Simple correlation identified two groupings of trace elements, with a possible relationship with weather, such as wind direction and speed. In order to clarify this relationship factor analysis was conducted upon the dataset. The factor analysis technique used was the same as that for C and Pb in Chapter 3 (14 variables were used with 104 degrees of freedom). Three separate factors were identified (Table 4.4).

Table 4.4

Factor analysis results of the trace element data with percentage variance aportionment (Ni and Cu were removed from the analysis due to an incomplete dataset). 14 variables were used with 104 degrees of freedom.

Factor 1 (36% variance)	Factor 2 (33% variance)	Factor 3 (23% variance)
Co, Cu and Mn	Al, Ba, Co, Cr, Mg, Mn, Ni, Pb, Sb , V, and rain.	Al and Wind direction.

Factor 1 consists of Co, Cu and Mn accounting for 36% of the variation at this site, approximately equal in importance to factor 2. These elements are all predominantly associated with wind-blown dusts (Table 4.4). This factor may represent a soil component which is not affected by the weather conditions monitored such as rain and wind direction. Thus, at this site the soil component is a continuous source of Co, Cu and Mn that does not derive from a particular location and is affected by other factors such as season and vegetative cover.

The factor 1 elements do not exhibit any relationship with wind direction, however. The maximum concentration values are consistent with higher average wind speed (2.1 to 2.8 ms^{-1}) than the minimum concentration values (0.8 to 1.8 ms^{-1}). This relationship with wind speed suggests that wind agitation and windblown dusts are important in generating and/or transporting elements within the atmosphere.

However there is evidence which indicates that wind-blown dust is not the only influencing source. For example, on the 17/6/92, a peak of Ni (6.41 ng ml^{-1}) and Zn concentration (35.6 ng ml^{-1}) occurred, with the increased presence of Zn concentration being indicative of a vehicle source. Thus the increased concentration in both Zn and Ni may indicate that on the 17/6/92 Ni was also derived from gasoline combustion (Nriagu and Davidson, 1986). It is suspected that the following days (19/5/92, 23/5/92, 22/6/92, 9/9/92, 15/9/92, 29/9/92,

23/10/92 and 15/1/93) the increase in element concentration can be attributed to windblown dusts of pre-deposited particulates.

Conversely, the minimum values of elements occur on dry days with low wind speeds (0.8 to 1.8 ms^{-1}) indicating that these elements depend upon wind transportation. These minimum values may thus represent the lack of re-working of previously deposited trace element particulates.

Factor 2 clearly identifies the influence of rain on the elements in this factor. This primary factor may represent a vehicle component in the Milton Keynes area and accounts for 33% of the variation at this site. This factor is a strong indication that these elements are "washed-out" of the atmosphere by rain.

Factor 2 elements all (except Pb) exhibit peaks in concentration values during rain episodes except on 16/2/93[1]. However, this is the inverse of the relationship between Pb concentration and rain. It is difficult to envisage a process that would increase the concentration of elements in the atmosphere during rain, unless precipitation was directly/indirectly involved in generating particulates. Such a process exists: simple mechanical agitation of pre-deposited material or for example, vegetation may increase the concentration of elements within the atmosphere. However, this would be a short-term process that would be rapidly masked by a prolonged episode of rain which would leach particulates from the atmosphere as washout. Thus precipitation would be directly responsible for an immediate increase in concentration during a short rain episode. Another indirect effect of rain on trace element concentration is the increased use of vehicles during rain, thereby increasing the supply of particulate trace elements into the atmosphere. This increase may outweigh the effect of particulate washout during rain.

The hypothesis that this factor represents a vehicle-derived component is supported by the fact that all trace elements except Ba in group 1[2] are associated with vehicles, *viz.* Al, Co,

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[1] *On the 16/2/93 there was no measurable wind speed and a smoky fire was noted on campus.*

[2] *Ni was not used in the factor analysis because of incomplete datasets.*

Cr, Mg, Mn, Pb, Sb and V[3]. Both Al and Mg are normally associated with a crustal/soil component but they also have vehicle influences; Cr and Mn have been associated with the accumulation of rust particles derived from vehicles (Hopke *et al.*, 1980); As, Ba, Cr and Mn are derived from tyre wear (Ondov, 1974; Hopke *et al.*, 1980); V is usually associated with fossil fuel combustion, but is also found in lubricants and heavy duty vehicle oils; Pb is primarily vehicle-derived.

Within factor 2 elements, a sub-division based upon concentration ranges is possible:

(a) Major elements which exhibit relatively high concentrations > 25.0 ng ml^{-1}: Al and Mg. Of this group, Mg is generated by vehicles: Mg accounts for 8.25% of road composite[4] and 1.25% of brake linings (Cass and McRae, 1983). These values are dwarfed by the carbon output some 56.2% and 87% carbon, respectively. The highly activated carbon particulates act as carriers for the elements. Thus, the elements for this group would be expected to show similar behaviour to carbon. However, Al only accounts for 0.34% of the vehicle aerosol (Cass and McRae, 1983). The most common source of Al is crustal; it is a major soil component (Nriagu and Davidson, 1986). Fugitive Al aerosols would be increased by the increase in traffic, which could re-inject material into the atmosphere.

(b) Trace elements which exhibit relatively low concentrations (< 25.0 ng ml^{-1}) are Ba, Co, Cr, Mn, Pb, Sb and V. Of the low concentration trace elements within factor 1, Cr, Pb, Sb and V are also mainly generated by vehicles; with Co being mainly generated by power plants, burning of domestic and industrial and refuse incineration, Cr and Ni (body), Pb (petrol vehicles) and Sb (oils and greases); V (diesel engines). Co is mainly generated by power plants, burning of domestic and industrial waste and refuse incineration. On the 9/7/92 and 9/10/92 the Open University incinerator was in operation. This coincides with high Co concentrations of 37.37 ng ml^{-1} and 42.86 ng ml^{-1}, respectively. The other two Co

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[3]*Mg accounts for 8.25% of road composite, as a percentage of chemical composition of fine aerosol emissions from highway vehicles.*

[4]*Percentage of chemical composition of fine aerosol emissions from highway vehicles.*

concentration of 3/7/92 and 17/9/92 may reflect the influence of the hospital incinerator[5], approximately 2 km northwest of the sample site.

The only element within this sub group that does not have a direct vehicle source is Ba. In fact paint is the dominant Ba source. It is therefore most probable that paint chips from vehicles and/or road markings are the main sources of Ba in this group. Thus, Ba particulates can be regularly introduced into the atmosphere by paint and road erosion and are directly related to vehicle sources and indicates that there is an association with other elements of this group. Therefore, factor 1 is believed to reflect the influence of vehicles on the generation of aerosols at the Milton Keynes site.

Factor 3 consists of Al and wind direction and accounts for 23% of the variation at this site. This association implies that Al is greatly influenced by wind direction.

Thus, the 3 trace element factors indicate that weather has a primary importance in influencing trace elements at the Milton Keynes site. For example factor 2 indicates that rain influences vehicle-derived particles and factor 3 suggests that wind direction affects the Al point source. However, not all variation of trace elements can be accounted for by weather. Factor 2 indicates that soil does not appear to be influenced by the weather conditions measured. These factors are quite different from the two groups identified by correlation and graphical analysis. However, the sources identified do not conflict. The high and low concentration sub-division of group 1 elements are accounted for by factor 1, the vehicle component (except for Co and Zn). Group 2 elements are found to lie in both factors 1 and 2, the vehicle and soil components. This element cross-factor distribution indicates that a two-group (source) model is too simplistic. A further division of trace element sources is achieved by factor analysis. Factor 3 established a relationship, between Al and wind direction, which was not apparent by simple correlation. Therefore simple correlation and graphical comparison were useful primary indicators of possible sources, with factor analysis contributing toward source identification and weather relationships.

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[5]*No data is available as to the content or concentration of incinerated material for bothe the Open University and the Milton Keynes hospital incinerator.*

Factor analysis does not indicate seasonality but suggests it with trace element and weather relationships for example, factors 2 and 3.

4.6.1 Seasonality

The elements within the factors identified indicated variations in seasonal concentration. Group 1 elements all exhibit increased concentration variability during September-December 1992 and April 1993, with relatively high concentrations. During the periods May-August 1992 and January-March 1993 these elements exhibit a variable concentration, with a reduction of Stdev and a decrease in average concentration (Figures 4.15 and 4.16). Winter concentrations appear to be variable, indicating a periodic output from sources, with sharp peaks in concentration on particularly cold and wet days. These meteorological conditions reflect the air mass trajectory and stability of the atmosphere (Dehairs *et al.*, 1982). For example, on both the 3/7/92 and 27/11/92 all elements in this group exhibited high concentrations. Rain was recorded throughout both these days, with simillar wind speeds and (2 to 2.4 ms^{-1} and 0.6 to 2.6 ms^{-1}, respectively). On the 27/11/92 the ambient temperatures was 7.5°C. Although the temperature was not particularly low for that time of year, it was cool in comparison to the previous week (23/11/92 = 15°C). Thus, during this week (23rd to 27/11/92) the temperature fell from 7.5 to 15°C, a considerable drop. This decrease in temperature coupled with rain reflects a more turbulent atmosphere. Simillar conditions were found on the 26th to 29/7/92. Winter concentrations of group 1 elements are thus identifiable by high and relatively variable concentrations which are influenced by weather conditions such as rain, wind speed and human behaviour. Actions such as increased use of vehicles during cold, wet days).

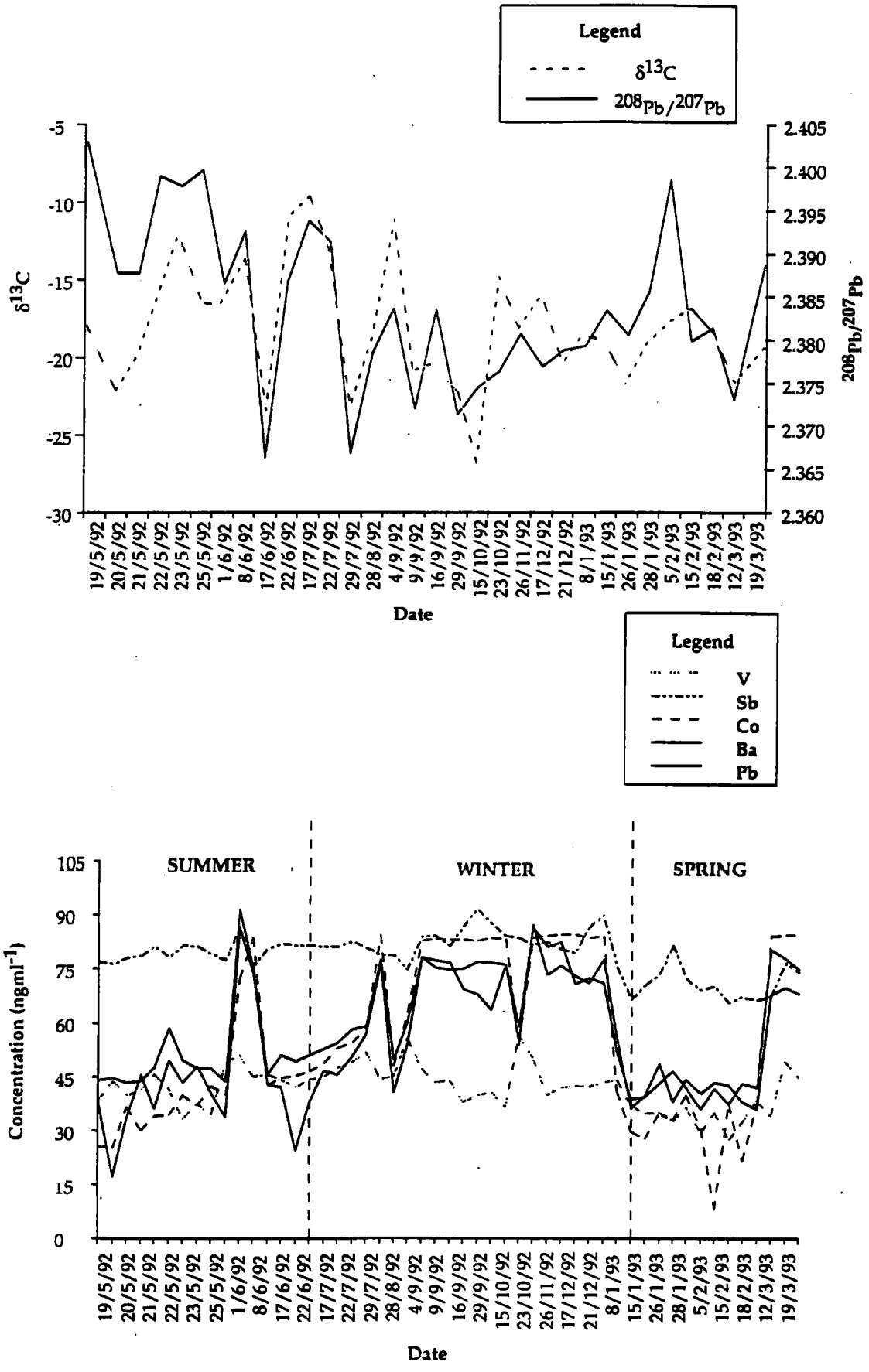

Figure 4.15
The relatively low concentration group 1 elements (V, Co, Ba, Sb and Pb) and isotopic compositions vary with time.

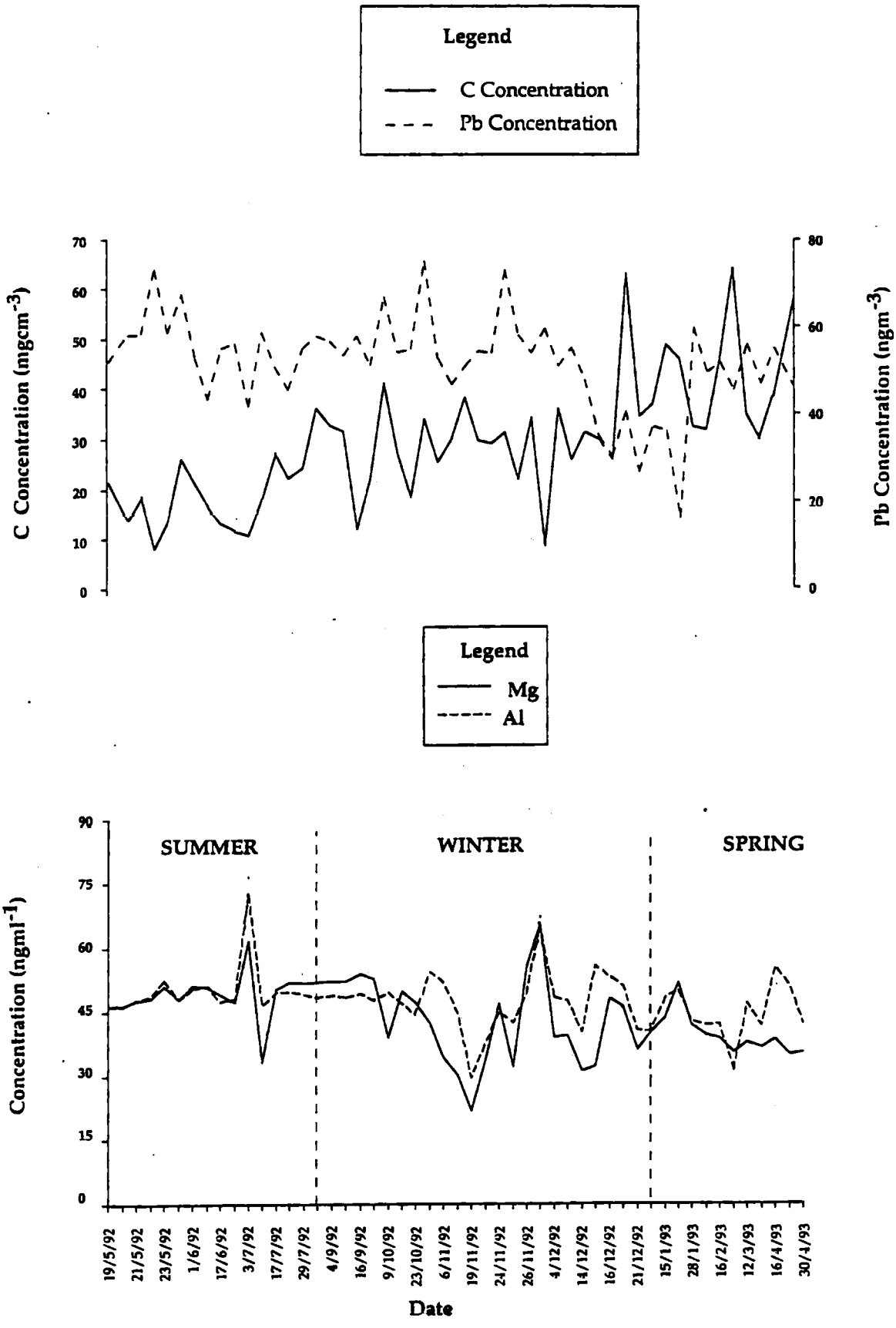

Figure 4.16.
Relatively high concentration factor 1 trace elements (Mg, Al and Zn), C and Pb vary with time.

The elements within Group 2 exhibit a seasonal duality with high and variable concentrations during the winter period (Sept-Dec 1992). During the summer period (May-August 1992) Cr, Mn and As exhibit lower concentrations that are relatively steady with Ni and Cu concentration being variable. This is not understood. The January to March 1993 concentration data were low and relatively constant. This period of low concentration may be indicative of the increase in temperature from 3.5 to 11.5°C, which may have lead to a decrease in combustion from power generating sources.

Also, average wind speeds[6] of 1.1 to 2 ms^{-1} may not be sufficient to agitate the pre-deposited particulates and re-incorporated into the atmosphere.

Therefore, during the winter months all element potential sources are of importance, for example vehicles and soil. Winter concentrations would be expected to be high. However, during the summer months the ambient temperature increases, reducing the requirement for domestic heating and decreasing soil input by increasing vegetative cover. Thus, during the summer months the net affect would be a reduction in element concentrations, with a dependence upon the re-incorporation of particulates into the atmosphere by wind agitation of the soil. The decrease in concentration and increased stability of values for January to March 1993 is associated with low mean wind speeds of 1.1 ms^{-1} and relatively high winter temperatures of 3.5 to 11.5°C. Thus, during this time the ambient temperatures were relatively high reducing combustion sources, with wind speeds being insufficient to re-incorporate particulates into the atmosphere. External variable(s) are thought to reflect the influence of weather conditions and/or anthropogenic factors. For example, during the winter there is a greater volume of traffic on the roads (Department of Transport, 1994), an increase in the burning of fuels (both residential and commercial) and a general increase in wind-blown material (decrease in vegetative cover of soil). These factors will all increase the available sources of particulates into the atmosphere and produce a variable C and Pb isotope signature (Figure 4.15).

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[6] *Excluding an unusually high wind speed of 7.3 to 10.7 ms^{-1} on the 15/1/93.*

Thus, during winter the trace elements would be expected to be relatively high and daily variations depending upon social factors, such as holidays, wet/dry days, or indicating specific outputs of local point sources, such as the University incinerator. These winter variations in trace elements and isotopic composition will further be influenced by weather conditions, for example rain episodes and wind. These conditions are further amplified by season.

Summer values exhibit steady lower concentrations and more stable C and Pb isotope values (Figures 4.15 and 4.16) which may represent a relative decrease in demand for heat (McDonald and Duncan, 1979) vehicle traffic and wind blown-dust. These sources are related to meteorological considerations such as wind speed and direction, air mass trajectories, rainfall, temperature, humidity and atmospheric stability (Moore, 1987; Gomez and Martin, 1987).

The similarity in seasonal variation between trace elements and isotopic compositions strongly indicates that these variations are not coincidental and do reflect real rhythmic seasonal variation. However, it is clear that much background 'noise' exists. This is mainly due to various environmental parameters, such as duration and intensity of wet and dry periods, wind direction, social and economic factors. The complex environmental relationship between trace element particulates, source, atmospheric transportation and deposition is further complicated by political-economic factors, such as an increase in the government road building policy, coupled with an environmental tax on leaded petrol, which encourages the increased use of roads and unleaded fuels (EEC, 1985).

4.7 Summary

Trace element data were analysed using factor analysis. Three main factors were identified indicating three separate source components: vehicles, soil and point sources (incinerators) components, accounting for 36%, 33% and 23% of the total variation. The percentage distribution between the components indicates that, for the mean Milton Keynes aerosol, vehicle and soil dust sources are of equal importance whereas point sources, such as incinerators, are less important. These component sources were found to vary with season. These seasonal variations are thought to be a result of fluctuations in both energy demand and meteorological factors, such as atmospheric stability and rainfall. The washout process has been identified as important to trace element concentration, with rainfall decreasing particulate concentration in air. Conversely, increasing wind speed was found to increase trace element concentrations. Thus, similar variation with summer/winter in trace elements have been identified in carbon and Pb data. These observations are further substantiated by trace element correlations with carbon and Pb isotopic data.

Chapter 5.

Conclusions and suggestions for future work

5.1 Introduction

This project has focused mainly upon the characterisation of aerosols and their sources by the analysis of carbon and Pb isotope ratios, trace element concentrations and meteorological parameters. The Milton Keynes dataset indicated large daily variations of carbon, Pb and trace element concentrations, which reflected the strong influences of meteorological conditions upon isotopic compositions and concentrations. If for example, rain occurs at the source and not at the receptor or *vice versa*, this would produce a large discrepancy in measured concentration. Similarly, wind direction and speed play an important role by controlling rates of transport from various source areas. However, despite these fluctuations the mean concentration values of carbon, Pb and trace elements are of similar magnitude to those observed by other workers (Migon *et al.*, 1993, Brémond *et al.*, 1989, Heintzenberg and Winkler, 1984).

The south Wales dataset indicated that there was a variation in carbon and Pb isotopic along the coast. It was possible to produce a preliminary characterisation of atmospheric particle sources: rural, marine and industrial. Wind direction and rain were found to influence particle mixing within the atmosphere, although these effects were more prominent in the Milton Keynes dataset.

5.2 Milton Keynes

The carbon and Pb isotopic compositions at Milton Keynes indicated that there were at least two distinct sources of atmospheric particles: soil and vehicle emissions. A Pb isotope mixing model (Model 1) supported the hypothesis that the local aerosol is composed of a mixture of particles of these two sources .

Carbon concentration and isotopic compositions were found to be useful in conjunction with Pb data. The $\delta^{13}C$ values range from -9.5 (±0.1) to -28.4 ‰ (±0.03). This range encompasses many carbon sources with $\delta^{13}C$ values (commonly at least 5 ‰ or more). For example, fossil fuels -23 to-28 ‰ (Court *et al.*, 1981 and Chesselet *et al.*, 1981) and vegetation -12 to -29 ‰ (Cachier *et al.*, 1985). Thus, it was difficult to characterise sources in terms of carbon isotope characteristics alone. However, when $\delta^{13}C$ values and Pb isotopic compositions are used in conjunction, particle source areas can be identified including local soils and vehicle emissions.

Meteorological factors such as rain and wind direction strongly influenced source composition and transportation and the mixing of aerosols. Weather exhibited a distinctive relationship with carbon and Pb isotopes and trace element concentration. Rain influenced both Pb concentration and isotopic composition: Pb concentration and isotope ratios in air decreased during a rain episode. This relationship reflects the nature of Pb particulates available during and immediately after rain. That is, vehicle emission-derived Pb particulates are generated and available throughout with other sources such as soil particles, requiring auxiliary transporting factors such as wind injection, in order to be incorporated into the atmosphere. The wind direction was also found to influence the source of atmospheric particulates. For example, northwest wind direction is thought to mainly represent soil particle emission sources, whereas a south-southwest wind direction represents mainly vehicle sources.

Thus, at Milton Keynes it is suggested that aerosol particles are a mix of soil and vehicle emission-derived particulates. During rain, particulates, particularly those containing Pb, are washed out of that atmosphere and produce a shift in the isotopic signature towards

vehicle-derived particles. This has been termed the "juvenile" aerosol. This "juvenile" aerosol is then mixed with other sources of particulates and eventually reaches the mean aerosol value for the site ($^{208}Pb/^{207}Pb$ = 2.389 ± 0.006). This is termed the "mature" aerosol.

Part of this work in Milton Keynes has focused on trace element concentration and used principal component analysis to identify sources and establish meteorological effects. Principal component analysis (PCA) is a powerful multivariate technique for relating a large dataset of elemental concentrations to possible source regions. Results for 11 trace elements were reduced to 3 components using PCA. The first component contains Mn, Co and Cu and represents the soil component source (accounting for 36 % of the variance). The second contains Al, Ba, Co, Cu, Mn, Ni, Pb, Sb and rain and represents the vehicle emissions component which accounts for 33% of the variance. The third contains Al and wind direction and represents 23% of the variance. This component represents the strong association of wind direction and Al concentration.

Carbon and Pb isotope data were also subjected to PCA and three components were identified. The first component accounts for 38% of the variance and contains $^{208}Pb/^{207}Pb$, $\delta^{13}C$ values, carbon concentration and rain. This component is thought to represent vehicle emissions. The second component accounts for 31% of the variance and contains $^{204}Pb/^{207}Pb$, and wind direction. This component is thought to represent soil influence. The third component accounts for 30.4 % of the variance and contains Pb concentration, wind direction and rain. This component is thought to represent meteorological influence.

The isotopic composition and trace element concentrations exhibit a marked seasonal variation which is probably due to both meteorological and emission patterns. For example, an inversion associated with an anticyclone can act as an effective blanket by inhibiting the vertical movement of pollution, thus entrapping it close to the surface and not allowing dispersal. Also, this process also cause the downward movement of warm, dry air reducing cloud formation and consequently, precipitation. Thus, this meteorological process would not only physically entrap pollution, but also reduce removal of aerosol particles by washout.

5.3 Wales

Wales 1991 data established that there is a variation of Pb isotopic composition along the coastline, with a preliminary Pb isotopic characterisation of aerosols (**marine, rural** and three separate **industrial** source areas). The 1992 and 1993 Welsh dataset further characterised these source areas.

The 1992 and 1993 data indicated that sources did indeed show annual variations with three distinct source areas: marine, industrial and rural. Two mixing zones have also been established: industrial/marine and vehicle/marine.

In order to verify the range and variety of sources in this region a multiple and simultaneous sampling regime would have to be implemented, with sample site density in the order of 5 km. This regime would clarify the range and influence of a particle source.

The south Wales data is clearly more difficult to synthesise than the Milton Keynes data, with both multiple sites and greater temporal variation in the collection of data. Therefore, only a crude preliminary characterisation of atmospheric particle sources can be accomplished. However, the ability to discriminate between natural marine and rural sources and anthropogenic particle sources, indicates that this analytical technique has great value in identifying carbon and Pb atmospheric particle sources.

5.4 Summary

The Milton Keynes site was established as possessing aerosols that are a mixture of vehicle emissions and soil-derived particulates. Meteorological factors such as rain and wind direction exhibited a strong influence upon source deposition and transportation. Underpinning these relationships are trace element data that also identifies soils and vehicle emissions as the major sources of particulates within the atmosphere at Milton Keynes, with rain and wind direction exerting influence upon concentration. For example, the vehicle component identified by principal component analysis is associated with rain. Therefore, the Milton Keynes study was a useful indicator of meteorological relationships with carbon and Pb isotope characteristics and trace element concentrations in aerosol particles and produced some useful insights into the generation, transportation and deposition of aerosols.

Wales carbon and Pb isotope data established 3 main source areas that remain relatively stable from year to year. The values at each site were found to be dependent upon wind direction which produced a mixing affect. For example, a north-westerly wind direction would be indicative of aerosols originating/transported over marine areas. North-westerly winds produce values close to Broadhaven seawater ($^{208}Pb/^{207}Pb = 2.394$). Modelling of Pb isotopic ratios indicates that the mixing of Broadhaven seawater and Rhoscrowther soil produce the sample values for north-westerly winds (Model 6 and Appendix B (V)).

Thus, it was possible to discriminate between natural (marine and rural) and anthropogenic particle sources. This characterisation of particles indicates that carbon and Pb isotopic analysis has great value in identifying sources of carbon and lead particles within the atmosphere. This technique may also be useful in refining element cycling models.

5.5 Recommendations for future work.

1. The size particle collected in this study, 5 to 0.5 μm, was chosen in order to collect both anthropogenic and natural particulates, while reducing particle size related variables. However, in future work the size distribution of particles should be investigated by collecting samples with a cascade impactor. This would distinguish between large and small particles and establish which specific sizes were responsible for transporting anthropogenic and natural particles.

2. Future work should also deal with the identification of source emissions for both the Milton Keynes and Welsh sites. Meteorological investigations should include air mass back-trajectories in order to establish specific source areas. For example, air mass trajectories could establish if isotopic variations and high trace element concentration events originated over the sea or in the UK.

3. The results obtained in this work are encouraging as a progression toward a better understanding of the relationships between element concentration and weather. Clarification of these issues requires a longer monitoring period, with input of data from additional sample stations and continuous sampling (for both air and precipitation). Moreover, the collection of wet deposition and air samples would help to determine the process of transport and deposition of carbon, Pb and trace element particles. Thus, in order to quantify atmospheric inputs to the Milton Keynes and South Wales areas, studies on rainfall and air samples over the Bristol Channel are necessary for the determination of fluxes and the factors controlling them.

4. Generally, future sampling programmes should include a more frequent sampling regime in order to link more directly ambient air concentrations with prevailing weather conditions. Daily sampling should be sufficient with a long-term monitoring programme

could also be undertaken in order to determine seasonal fluxes and account for annual climate variability.

5. The same suggestions for future sampling programmes are recommended for the south Wales sites. In particular, in this region it would be beneficial to ascertain if seasonal variation exists in the source areas. In order to identify any such seasonal variation it would be necessary to initiate a daily sampling programme for a number of years. In addition the collection of trace element data would be useful in order to compare with the isotopically identified marine, urban and rural zones. Future isotopic studies should measure and further characterise local sources, for example local biogenic and industrial sources.

6. A further suggestion for future work is the collection of particulate air samples from other remote areas around the UK. Specifically, isolated rural areas and the identification of key east and west coast marine source areas. Such a sampling regime would establish any geographical source variation within the UK.

7. In recent years, Polycyclic Aromatic Hydrocarbons (PAHs) have become of concern because they have been demonstrated to be both carcinogenic and mutagenic (Arey *et al.*, 1987, Lewats *et al.*, 1987, Motykicwicz *et al.*, 1988, Tuominen *et al.*, 1988). The effect on humans has led to PAHs being widely studied (Harkov and Greenberg, 1985; Greenberg *et al.*, 1985 Baek *et al.*, 1991; Baek *et al.*, 1992 and Takada *et al.*, 1991). PAHs are the products of incomplete combustion of hydrocarbons and are naturally present in vegetation and fossil fuels. However, anthropogenic sources are of greater importance.

   PAHs are predominantly associated with particulate matter (National Academy of Sciences US, 1972). PAHs are generated in the gas phase and then adsorbed on or incorporated into particles while undergoing condensation upon further cooling (Thomas *et al.*, 1963 and Van Vaeck *et al.*, 1984). Because PAHs in the atmosphere are closely associated with particulate matter, their atmospheric residence time is

closely related to the behaviour of the carrier particles (McVeety and Hites, 1988, Chuang *et al.*, 1987, Baker and Eisenreich, 1990).

The physical removal or transportation of particles are related to the size and meteorological conditions. Thus, particles which carry PAHs have characteristics similar to those measured in trace element particles. Isotopic characterisation of process-specific PAHs would aid in the identification of both anthropogenic and natural sources.

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Appendix A (i)

A table of Pb sampling apparatus percentage consistency.*

Date	Conc of Pb in 1M HBr (ng/m^3)	% Sampling consistency*	Date	Conc of Pb in 1M HBr (ng/m^3)	% Sampling consistency
29-1-92	0.21	86	27-11-92	0.05	93
5-2-92	0.45	73	4-12-92	0.08	82
19-5-92	0.05	61	9-12-92	0.04	59
20-5-92	0.05	60	14-12-92	0.05	83
22-5-92	0.47	52	15-12-92	0.03	50
23-5-92	0.08	88	21-12-92	0.01	56
25-5-92	0.24	48	15-1-93	0.007	48
1-6-92	0.04	78	18-1-93	0.05	78
17-6-92	0.06	62	26-1-93	0.006	91
22-6-92	0.06	100	29-1-93	0.06	88
9-7-92	0.07	82	30-1-93	0.04	96
29-7-92	0.06	99	5-2-93	0.1	100
9-9-92	0.05	84	12-2-93	0.007	62
16-9-92	0.04	52	15-2-93	0.005	59
29-9-92	0.04	50	18-2-93	0.04	69
9-10-92	0.31	71	21-2-93	0.03	80
15-10-92	0.05	87	19-3-93	0.06	82
23-10-92	0.09	63	Max	0.47	100
6-11-92	0.04	78	Min	0.005	48
20-11-92	0.04	78	Average	0.09	74
26-11-92	0.12	70	StDev	0.13	16

The sampling consistency is in the range of 48 to 100%. Where the percentage of consistency is low and daily variation is high the data becomes difficult to interprete. Where this situation occurs the issue is highlighted in the text.

*Sampling consistency = percentage difference between the first and second air sample taken (assuming all environmental conditions being equal). Thus, consistancy was used as a measure of reproducability.

Appendix A (ii)

Open university total procedure blanks (TPB) and blank corrected lead values

Name	Date	Pb conc (pg/ml)	±	$^{207}Pb/^{204}Pb$	±	$^{204}Pb/^{206}Pb$	±	$^{208}Pb/^{207}Pb$	±
TPB	20/2/91	6.72	0.0520	0.03614	0.00037	0.06595	0.00069	2.37817	0.00063
TPB	1/3/91	4.87	0.0670	0.09919	0.00046	0.06475	0.00029	2.35817	0.00090
TPB	27/3/91	4.87	0.0680	0.09566	0.00003	0.06452	0.00021	2.37936	0.00152
TPB	24/4/91	0.60	0.0600	0.19547	0.01116	0.06473	0.00021	2.38114	0.00147
TPB	3/5/91	4.80	0.0270	0.09559	0.00003	0.06471	0.00093	2.37903	0.00093
TPB	4/3/92	2.27	0.0250	0.31169	0.00005	0.06377	0.00015	2.37368	0.00056
TPB	14/13/92	0.13	0.0300	0.09762	0.00006	0.06382	0.00016	2.37123	0.00062
TPB	25/4/92	0.47	0.0680	0.09541	0.00009	0.06515	0.00076	2.35843	0.00146
TPB	17/6/92	2.27	0.0120	0.31169	0.00005	0.06377	0.00015	2.37368	0.00056
TPB	1/3/93	0.20	0.0280	0.09562	0.00006	0.06382	0.00010	2.37641	0.00021
TPB	5/4/93	18.73	0.0720	0.13457	0.00006	0.06461	0.00071	2.35632	0.00064
TPB	18/5/93	22.33	0.0510	0.17216	0.00003	0.06328	0.00082	2.33812	0.00023
TPB	28/6/93	33.40	0.0680	0.09322	0.00003	0.06392	0.00074	2.35622	0.00064
	Stdv	20.79	0.0210	0.08535	0.00307	0.00072	0.00032	0.01300	0.00044
	Average	7.82	0.0483	0.14108	0.00096	0.06437	0.00046	2.36769	0.00080

Appendix A (iii)

Fractionation correction factors for NBS981.

Where:

R = real value

Rm = measured value

E = mass difference per mass unit

dm = mass difference

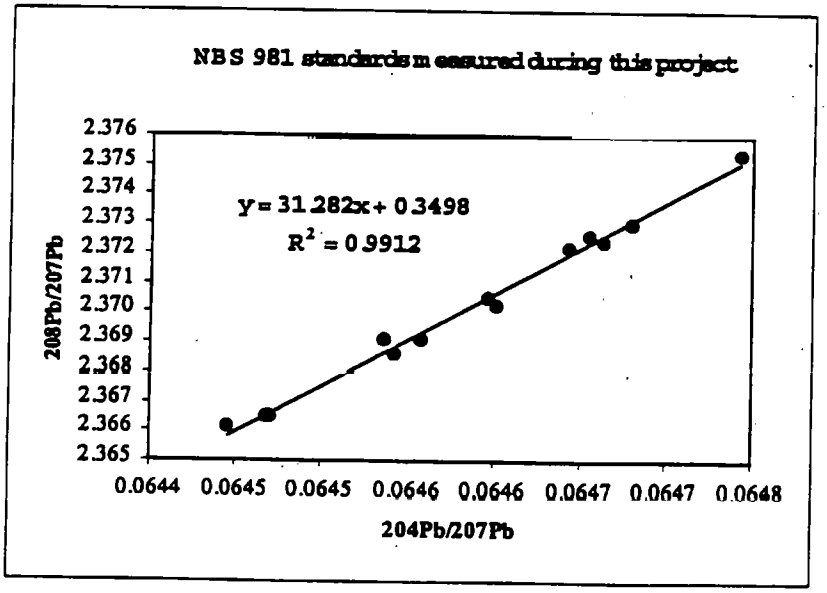
Date	Rm $^{206}Pb/^{207}Pb$	Error	Rm $^{204}Pb/^{207}Pb$	Error	Rm $^{208}Pb/^{207}Pb$	Error	E $^{206}Pb/^{207}Pb$	E $^{204}Pb/^{207}Pb$	E $^{208}Pb/^{207}Pb$
2/20/91	1.0932	0.0162	0.0645	0.0175	2.3665	0.0391	1.0933	0.0646	2.3692
3/1/91	1.0936	0.0063	0.0646	0.01	2.3702	0.0207	1.0933	0.0646	2.3692
3/27/91	1.0934	0.0156	0.0646	0.0389	2.3705	0.0389	1.0933	0.0646	2.3692
1/20/92	1.0931	0.0037	0.0646	0.0037	2.3691	0.0082	1.0933	0.0646	2.3692
4/12/92	1.0934	0.1724	0.0644	0.2102	2.3661	0.4924	1.0933	0.0646	2.3692
5/16/92	1.0934	1.0032	0.0645	1.4973	2.3665	2.5006	1.0933	0.0646	2.3692
6/13/92	1.0943	0.0147	0.0647	0.0194	2.3754	0.0084	1.0933	0.0646	2.3692
6/17/92	1.0935	0.5396	0.0645	0.5549	2.3691	1.2696	1.0933	0.0646	2.3692
7/14/92	1.0934	0.0042	0.0645	0.005	2.3686	0.0138	1.0933	0.0646	2.3692
10/11/92	1.0936	0.0017	0.0646	0.002	2.3722	0.0032	1.0933	0.0646	2.3692
12/12/92	1.0937	0.0009	0.0647	0	2.3726	0.0027	1.0933	0.0646	2.3692
3/19/93	1.0937	0.0149	0.0647	0.02	2.373	0.0529	1.0933	0.0646	2.3692
5/2/93	1.0937	0.0018	0.0647	0.0019	2.3724	0.0051	1.0933	0.0646	2.3692

Date	dm $^{206}Pb/^{207}Pb$	dm $^{204}Pb/^{207}Pb$	dm $^{208}Pb/^{207}Pb$	R $^{206}Pb/^{207}Pb$	R $^{204}Pb/^{207}Pb$	R $^{208}Pb/^{207}Pb$
2/20/91	1	3	1	2.2884	0.077	19.1868
3/1/91	1	3	1	2.2892	0.0771	19.2172
3/27/91	1	3	1	2.2889	0.0771	19.2196
1/20/92	1	3	1	2.2882	0.0771	19.2076
4/12/92	1	3	1	2.2889	0.0769	19.184
5/16/92	1	3	1	2.2889	0.077	19.1871
6/13/92	1	3	1	2.2908	0.0773	19.2592
6/17/92	1	3	1	2.289	0.077	19.208
7/14/92	1	3	1	2.2888	0.077	19.2041
10/11/92	1	3	1	2.2892	0.0772	19.2329
12/12/92	1	3	1	2.2895	0.0772	19.2366
3/19/93	1	3	1	2.2895	0.0772	19.2397
5/2/93	1	3	1	2.2895	0.0772	19.2347

Appendix A (iii)

Fractionation correction factors for NBS981 (continued).

$^{206}Pb/^{207}Pb$ Std	$^{204}Pb/^{207}Pb$ Std	$^{208}Pb/^{207}Pb$ Std	$^{206}Pb/^{207}Pb$ Correction Factor	$^{204}Pb/^{207}Pb$ Correction Factor	$^{208}Pb/^{207}Pb$ Correction Factor
2.2884	0.0771	19.2092	0.0001	0.0001	-0.0224
2.2892	0.0771	19.2092	-0.0001	-0.0001	0.0079
2.2889	0.0771	19.2092	0	0	0.0103
2.2882	0.0771	19.2092	0	0	-0.0016
2.2889	0.0771	19.2092	0.0001	0.0001	-0.0252
2.2889	0.0771	19.2092	0.0001	0.0001	-0.0221
2.2908	0.0771	19.2092	-0.0002	-0.0002	0.05
2.289	0.0771	19.2092	0	0	-0.0013
2.2888	0.0771	19.2092	0	0	-0.0052
2.2892	0.0771	19.2092	-0.0001	-0.0001	0.0237
2.2895	0.0771	19.2092	-0.0001	-0.0001	0.0274
2.2895	0.0771	19.2092	-0.0002	-0.0002	0.0305
2.2895	0.0771	19.2092	-0.0001	-0.0001	0.0255
		Min	**-0.0002**	**-0.0002**	**-0.0252**
		Max	**0.0001**	**0.0001**	**0.05**
		Stdev	**0.0001**	**0.0001**	**0.0232**
		Mean	**0**	**0**	**0.0075**



Appendix A (iv)

Tabulated Blank Results: 30 ml 1M HBr Blank

Name	Date	Pb concentration (pg/ml)	±
HBr1M 30 ml	18/3/87	51.03	0.06
HBr1M 30 ml	24/4/87	52.29	0.05
HBr1M 30 ml	22/4/87	23.06	0.01
HBr1M 30 ml	11/4/87	44.24	0.04
HBr1M 30 ml	2/5/87	22.42	0.06
HBr1M 30 ml	3/3/88	16.00	0.02
HBr1M 30 ml	13/3/88	88.12	0.08
HBr1M 30 ml	24/4/88	100.00	0.09
HBr1M 30 ml	14/9/88	30.60	0.01
HBr1M 30 ml	28/2/89	40.71	0.07
HBr1M 30 ml	4/4/89	39.56	0.04
HBr1M 30 ml	15/5/89	81.70	0.03
HBr1M 30 ml	27/6/89	61.58	0.05
Stdv		**52.74**	**0.05**
Average		**50.10**	**0.06**

Tabulated Blank Results: 15 ml 0.5M HBr Blank

Name	Date	Pb concentration (ng/ml)	±
HBr 15ml 0.5M	14/2/87	0.72	0.005
HBr 15ml 0.5M	28/2/87	1.13	0.02
HBr 15ml 0.5M	13/3/87	1.94	0.003
HBr 15ml 0.5M	26/3/87	10.60	0.02
HBr 15ml 0.5M	20/4/87	1.03	0.008
HBr 15ml 0.5M	23/4/87	63.74	0.043
HBr 15ml 0.5M	23/4/87	0.93	0.061
HBr 15ml 0.5M	23/4/87	1.35	0.05
Stdv		**43.79**	**0.04**
Average		**10.18**	**0.03**

Tabulated Blank Results: 15 ml 1M HBr Blank

Name	Date	Pb concentration (pg/ml)	±
HBr 1M 15 ml	13/3/87	18.90	0.03
HBr 1M 15 ml	13/3/87	13.50	0.5
HBr 1M 15 ml	18/3/87	24.70	0.03
HBr 1M 15 ml	18/3/87	1.03	0.5
HBr 1M 15 ml	22/4/87	6.23	0.2
HBr 1M 15 ml	2/5/87	31.23	0.08
HBr 1M 15 ml	29/4/88	103.00	0.6
HBr 1M 15 ml	27/4/88	93.00	0.5
HBr 1M 15 ml	26/5/88	106.00	0.04
HBr 1M 15 ml	22/3/88	63.70	0.1
HBr 1M 15 ml	29/6/89	40.00	0.02
HBr 1M 15 ml	4/3/89	72.00	0.2
Stdv		76.54	0.4
Average		47.77	0.2

Tabulated Blank Results: 30 ml 0.5 M HBr Blank

Name	Date	Pb concentration (ng/ml)	±
HBr 0.5M 30 ml	18/2/87	1.33	0.2
HBr 0.5M 30 ml	28/2/87	2.64	0.006
HBr 0.5M 30 ml	11/3/87	15.60	0.07
HBr 0.5M 30 ml	13/3/87	6.15	0.1
HBr 0.5M 30 ml	26/3/87	5.36	0.2
HBr 0.5M 30 ml	26/3/87	1.68	0.2
HBr 0.5M 30 ml	20/4/87	5.60	0.2
HBr 0.5M 30 ml	20/4/87	3.74	0.2
Stdv		9.11	0.2
Average		5.26	0.2

Tabulated Blank Results: 2TD15 ml HNO_3 Blank

Name	Date	Pb concentration (pg/ml)	±
2TD HNO_3 15ml	18/2/87	122.00	0.07
2TD HNO_3 15ml	28/2/87	80.24	0.3
2TD HNO_3 15ml	26/3/87	85.72	0.5
2TD HNO_3 15ml	23/4/87	123.00	0.3
2TD HNO_3 15ml	2/5/87	60.40	0.4
2TD HNO_3 15ml	3/3/88	72.60	0.06
2TD HNO_3 15ml	13/3/88	77.50	0.2
2TD HNO_3 15ml	24/4/88	63.70	0.3
2TD HNO_3 15ml	14/9/88	58.80	0.3
2TD HNO_3 15ml	28/2/89	300.00	0.4
2TD HNO_3 15ml	4/4/89	106.00	0.5
2TD HNO_3 15ml	15/5/89	67.50	0.03
2TD HNO_3 15ml	17/5/89	76.30	0.2
2TD HNO_3 15ml	27/6/89	51.30	0.3
Stdv		**125.59**	**0.2**
Average		**96.08**	**0.3**

Tabulated Blank Results: 15 ml 6M HCl Blank

Name	Date	Pb concentration (pg/ml)	±	207Pb/206Pb	±
6M 2TD HCl 15ml	18/2/87	59.70	0.03	0.0174	0.0003
6M 2TD HCl 15ml	28/2/87	58.40	0.08	0.0285	0.0004
6M 2TD HCl 15ml	26/3/87	16.05	0.2	0.0042	0.0008
6M 2TD HCl 15ml	23/4/87	57.22	0.6	0.0118	0.0001
6M 2TD HCl 15ml	2/5/87	104.93	0.5	0.0219	0.0002
6M 2TD HCl 15ml	3/3/88	105.00	0.3	0.0112	0.0001
6M 2TD HCl 15ml	13/3/88	16.32	0.2	0.0064	0.0006
6M 2TD HCl 15ml	24/4/88	200.00	0.1	0.0196	0.0008
6M 2TD HCl 15ml	14/9/88	13.56	0.4	0.0055	0.0009
6M 2TD HCl 15ml	28/2/89	13.66	0.4	0.0113	0.0006
6M 2TD HCl 15ml	4/4/89	610.00	0.1	0.0215	0.0007
6M 2TD HCl 15ml	4/4/89	52.60	0.6	0.0200	0.0001
6M 2TD HCl 15ml	15/5/89	60.50	0.5	0.0143	0.004
6M 2TD HCl 15ml	17/5/89	31.50	0.6	0.0168	0.002
Stdv		**155.12**	**0.2**	**0.0070**	**0.003**
Average		**99.96**	**0.3**	**0.0150**	**0.0004**

Appendix A (v)

Trace element clean room blank data (pg/ml).

Sample	Al	As	Ba	Co	Cr	Cu	Mg	Mn	Ni	Pb	Sb	Sn	V	Zn
Clean room blank	557	43	80	82.8	426	436	66.8	141	1829	65	2440	90	0.6	321
Clean room blank	553	27	107	52	449	440	58	75	1875	39	800	113	0.3	247
Clean room blank	550	36	149	74	373	601	62.6	101	2218	31	2140	196	0.3	409
Clean room blank	655	21	173	77.9	432	551	102	69	2175	57	2360	152	0.4	348
Clean room blank	637	31	190	47.6	417	415	102	89	2098	32	1620	81	0.5	382
Clean room blank	639	22	151	60.8	467	389	105	87	1800	52	1400	106	0.7	459
Min	550	21	80	47.6	373	389	58	69	1800	31	800	81	0.3	247
Max	655	43	190	82.8	467	601	105	141	2218	65	2440	196	0.7	459
Mean	599	30	142	65.9	427	472	82.7	93	1999	46	1793	123	0.5	361
Stdv	49.9	8.3	41	14.5	32	84	22.4	26	186	14	637	44	0.2	74

Trace element clean room HBr blank data (pg/ml).

Sample	Al	As	Ba	Co	Cr	Cu	Mg	Mn	Ni	Pb	Sb	Sn	V	Zn
HBr blank	457	18	78	111	308	101	18.4	55	1423	16	1132	7.9	0.1	232
HBr blank	448	47	74	129	319	174	20.9	61	1513	1.3	464	16	0.4	275
HBr blank	456	47	51	106	346	116	17.5	62	1605	2.9	772	16	0.3	303
HBr blank	504	11	54	106	367	230	19.4	70	2081	4.5	2680	28	0.3	237
HBr blank	505	101	37	73.9	367	223	19.9	95	1837	1.9	670	14	0.9	222
HBr blank	496	51	44	147	364	120	23.2	67	1591	7.4	206	29	0.4	234
HBr blank	457	21	134	76.2	401	148	21.4	65	1788	13	1158	152	0.2	282
HBr blank	513	34	88	74.3	353	190	24.7	77	2098	7.4	740	54	0.3	314
HBr blank	488	26	101	132	425	166	24.4	76	2152	5.9	474	146	0.3	217
Min	448	11	37	73.9	308	101	17.5	55	1423	1.3	206	7.9	0.1	217
Max	513	101	134	147	425	230	24.7	95	2152	16	2680	152	0.9	314
Mean	480	40	73	106	361	163	21.1	70	1788	6.6	922	51	0.4	257
Stdv	25.7	27	31	27	36	46	2.57	12	273	4.8	727	57	0.2	37

Appendix B (i)

Open University Trace element data (ng/ml).

Date	Al (ng/ml)	Ba (ng/ml)	Co (ng/ml)	Cr (ng/ml)	Cu (ng/ml)	Mg (ng/ml)	Mn (ng/ml)	Ni (ng/ml)	Pb (ng/ml)	Sb (ng/ml)	V (ng/ml)	Zn (ng/ml)	Wind Dir	Wind Speed (m/s)	Dry Temp	Wet Temp	Relative humidity (%)	Rain
18/5/92	12.13	0.1	0.5	1.5	15.6	12.5	1.7	14.3	3.6	13.6	3.6	40.2	80	3.2-2.4	25.5	21.0	65.0	2
19/5/92	12.19	0.1	0.5	2.0	2.2	12.5	2.0	12.1	0.1	12.1	8.4	5.4	80	2.2-1.8	21.0	19.0	85.0	2
20/5/92	15.66	0.1	2.8	2.4	2.5	15.3	4.4	13.0	1.7	16.1	4.5	67.1	70	1.3-0.8	21.0	18.0	75.0	2
21/5/92	17.53	0.1	0.0	2.3	1.7	16.3	0.5	9.2	10.6	17.2	5.7	11.1	180	2.4-1.3	22.0	16.5	55.0	2
22/5/92	31.06	0.2	1.8	3.5	7.4	25.0	9.3	11.6	2.6	26.1	10.8	25.9	40	2.4-1.2	13.5	14.5	90.0	2
24/5/92	15.86	0.8	2.0	1.7	1.9	15.7	8.6	6.9	20.0	16.5	5.9	9.4	340	0.6-0.1	22.0	17.5	65.0	2
31/5/92	23.19	0.2	4.4	2.8	3.3	25.9	18.5	4.8	7.5	26.7	1.6	11.0	320	0.6-0.1	17.0	16.5	95.0	0
8/6/92	25.19	0.1	2.9	3.1	1.4	24.6	5.6	8.3	15.3	25.3	3.2	65.9	220	3-2.4	23.0	20.0	75.0	2
16/6/92	14.39	0.1	6.8	3.3	2.7	19.2	10.9	64.1	4.9	18.7	1.9	35.6	28	1.9-0	18.0	13.0	55.0	2
21/6/92	16.33	0.1	4.4	3.5	13.9	13.9	8.2	11.1	1.8	14.4	17.4	42.5	120	2.3-1.1	20.0	15.5	65.0	0
2/7/92	76.51	12.4	6.5	No Reading	No Reading	127.6	No Reading	No Reading	57.9	57.0	25.1	12.9	90	2.4-2	14.5	14.5	100.0	0
8/7/92	12.60	10.8	37.3	No Reading	No Reading	1.7	No Reading	No Reading	7.8	11.2	10.0	36.9	220	1.5-0.5	18.5	16.5	85.0	2
16/7/92	19.93	0.1	6.9	4.5	4.9	22.5	11.4	11.5	6.9	23.3	10.9	10.6	300	2.5-1.2	18.5	16.5	80.0	1
19/7/92	15.80	0.2	10.3	2.2	16.9	26.1	25.6	No Reading	6.5	No Reading	7.1	46.0	120	1.5-1.0	20.5	15.5	65.0	1
21/7/92	20.33	0.2	9.4	4.2	16.6	29.5	17.8	10.5	6.5	28.7	8.6	46.0	60	2.4-0	23.0	16.5	50.0	2
28/7/92	19.06	0.2	10.2	4.8	34.1	28.7	20.6	11.9	0.4	26.8	6.4	45.9	40	0.5-0	20.0	16.0	65.0	1

Appendix B (I) *(continued)*

Open University Trace element data (ng/ml).

Date	Al (ng/ml)	Ba (ng/ml)	Co (ng/ml)	Cr (ng/ml)	Cu (ng/ml)	Mg (ng/ml)	Mn (ng/ml)	Ni (ng/ml)	Pb (ng/ml)	Sb (ng/ml)	V (ng/ml)	Zn (ng/ml)	Wind Dir	Wind Speed (m/s)	Dry Temp	Wet Temp	Relative humidity (%)	Rain
26/8/92	16.79	0.2	12.2	7.0	3.0	29.0	23.9	9.8	3.3	27.0	8.8	68.0	280	3.9-1.4	18.0	15.5	75.0	0
3/9/92	18.39	0.3	17.4	8.9	3.8	30.7	3.6	14.1	12.7	25.4	10.1	93.5	320	4.2-3.8	12.0	10.0	80.0	1
8/9/92	17.13	0.4	33.6	17.7	3.3	30.7	5.1	17.9	10.6	25.7	14.5	14.9	310	2.1-1.0	17.0	15.0	80.0	2
14/9/92	15.00	0.8	35.4	11.4	16.9	29.1	8.3	7.2	24.4	No Reading	19.9	18.2	60	2.0-3.0	16.0	11.0	55.0	2
15/9/92	19.79	0.7	42.1	12.3	15.2	39.6	6.6	13.5	23.9	31.3	18.8	20.3	60	3-2.1	16.0	11.0	60.0	2
16/9/92	22.40	15.7	37.4	No Reading	No Reading	11.3	No Reading	No Reading	10.7	10.9	7.5	39.7	70	16.50	14.0	75.0	75.0	2
28/9/92	15.33	0.9	77.8	21.0	2.0	32.7	5.8	24.9	60.7	24.6	28.3	16.7	240	2-1.1	16.5	15.0	85.0	2
8/10/92	20.07	15.1	42.9	No Reading	No Reading	4.1	No Reading	No Reading	12.4	17.6	8.9	16.4	60	2.8-3.2	12.5	9.5	65.0	2
14/10/92	13.59	0.2	16.4	9.1	2.4	21.2	2.9	15.3	5.0	17.9	10.5	8.8	160	3.4-2.8	5.0	4.0	85.0	1
22/10/92	8.86	1.0	1.5	21.6	1.4	13.9	10.5	38.8	38.5	9.7	52.5	20.0	260	3-2.6	7.5	6.0	95.0	1
29/10/92	42.20	16.2	33.2	No Reading	No Reading	6.6	No Reading	No Reading	16.2	40.5	14.1	17.9	No wind	0.00	8.5	7.0	85.0	2
5/11/92	29.87	10.7	36.5	No Reading	No Reading	2.0	No Reading	No Reading	14.3	41.8	8.0	17.8	320	2.6-1.6	16.0	14.0	80.0	1
12/11/92	9.67	9.7	35.3	No Reading	No Reading	1.0	No Reading	No Reading	13.2	26.7	8.8	17.0	220	0.6-0	4.5	2.5	70.0	1

Appendix B (I) *(continued)*

Open University Trace element data (ng/ml).

Date	Al (ng/ml)	Ba (ng/ml)	Co (ng/ml)	Cr (ng/ml)	Cu (ng/ml)	Mg (ng/ml)	Mn (ng/ml)	Ni (ng/ml)	Pb (ng/ml)	Sb (ng/ml)	V (ng/ml)	Zn (ng/ml)	Wind Dir	Wind Speed (m/s)	Dry Temp	Wet Temp	Relative humidity (%)	Rain
18/11/92	0.93	10.0	34.5	No Reading	No Reading	0.3	No Reading	No Reading	4.3	62.2	3.4	11.8	220	0-1.0	3.5	2.5	80.0	1
21/11/92	16.76	50.6	26.4	No Reading	No Reading	27.5	No Reading	No Reading	39.5	160.9	12.9	156.7	160	2.2-3.6	15.0	14.0	90.0	1
22/11/92	3.33	13.6	32.9	No Reading	No Reading	1.8	No Reading	No Reading	3.4	130.4	4.6	21.6	220	2.2-1.8	10.5	8.0	70.0	1
23/11/92	10.00	13.1	38.8	No Reading	No Reading	13.7	No Reading	No Reading	1.7	70.6	5.4	20.9	220	2.2-3.6	10.5	8.0	70.0	1
24/11/92	6.73	12.1	36.6	No Reading	No Reading	1.4	No Reading	No Reading	12.1	41.1	2.8	11.8	220	2.6-3.3	8.0	6.5	80.0	1
25/11/92	19.73	0.9	39.5	12.4	3.0	50.3	7.1	9.4	43.0	37.6	59.2	16.6	220	3.3-2.6	10.0	7.5	80.0	1
26/11/92	22.39	57.9	38.7	No Reading	No Reading	24.3	No Reading	No Reading	68.0	28.1	23.1	31.1	230	3.9-1.7	11.0	8.5	80.0	0
3/12/92	16.67	25.1	41.7	No Reading	No Reading	4.1	No Reading	No Reading	7.9	32.2	4.7	25.5	220	3.2-1.9	6.5	4.5	85.0	1
8/12/92	15.33	32.3	44.0	No Reading	No Reading	4.3	No Reading	No Reading	11.6	23.1	6.4	31.4	240	0-0.3	5.5	5.0	85.0	1
13/12/92	4.87	5.2	43.6	No Reading	No Reading	1.2	No Reading	No Reading	7.4	19.6	7.1	19.6	260	3.0-2.3	9.5	8.0	80.0	2
14/12/92	52.13	7.0	38.5	No Reading	No Reading	1.4	No Reading	No Reading	5.6	58.7	6.8	22.8	260	2.9-3.3	8.0	7.0	90.0	2

Appendix B (I) *(continued)*

Open University Trace element data (ng/ml).

Date	Al (ng/ml)	Ba (ng/ml)	Co (ng/ml)	Cr (ng/ml)	Cu (ng/ml)	Mg (ng/ml)	Mn (ng/ml)	Ni (ng/ml)	Pb (ng/ml)	Sb (ng/ml)	V (ng/ml)	Zn (ng/ml)	Wind Dir	Wind Speed (m/s)	Dry Temp	Wet Temp	Relative humidity (%)	Rain
15/12/92	35.67	5.4	42.4	No Reading	No Reading	16.5	No Reading	No Reading	15.4	101.9	8.0	40.0	260	0.0-0.5	5.5	5.0	90.0	0
16/12/92	24.99	0.3	5.7	3.1	3.3	11.9	36.4	18.1	55.1	11.7	9.1	11.0	120	1-0.5	8.5	5.0	70.0	0
20/12/92	5.26	0.0	0.9	1.4	0.0	2.6	6.8	7.4	2.7	2.7	2.9	7.9	28	1.2-1.0	0.0	0.5	95.0	2
7/1/93	4.93	0.0	0.7	1.0	0.1	4.8	17.4	9.0	4.4	5.0	2.1	97.1	260	2.3-1	7.0	5.0	65.0	2

Appendix B (I) *(continued)*

Trace element clean room blank data (pg/ml).

Date	Al (ng/ml)	Ba (ng/ml)	Co (ng/ml)	Cr (ng/ml)	Cu (ng/ml)	Mg (ng/ml)	Mn (ng/ml)	Ni (ng/ml)	Pb (ng/ml)	Sb (ng/ml)	V (ng/ml)	Zn (ng/ml)	Wind Dir	Wind Speed (m/s)	Dry Temp	Wet Temp	Relative humidity (%)	Rain
14/1/93	16.39	0.1	2.2	1.7	0.6	8.1	5.9	33.6	17.9	8.1	2.2	21.8	240	10.7-7.3	11.5	7.5	55.0	0
25/1/93	21.66	0.1	1.6	2.4	1.6	27.9	5.1	10.7	3.5	28.5	1.5	32.9	240	2.1-1.9	3.5	1.5	70.0	0
27/1/93	7.33	0.1	4.6	2.5	0.4	6.2	6.2	13.4	9.1	6.8	2.8	10.6	280	3.2-2.1	8.0	7.0	90.0	1
4/2/93	6.13	0.0	1.1	1.9	0.1	4.3	1.2	10.5	0.0	4.0	0.9	1.7	240	3-2.6	5.5	4.5	85.0	1
15/2/93	6.53	0.1	0.0	1.9	0.3	3.9	1.6	14.6	7.8	4.7	2.2	17.3	260	0.8-0.6	8.5	7.5	85.0	1
16/2/93	1.20	0.0	3.3	0.7	0.2	2.3	0.4	7.2	7.0	No Reading	0.7	15.2	260	0.00	8.5	6.5	85.0	1
11/3/93	13.39	0.1	0.3	1.1	0.2	3.3	5.2	10.5	3.5	3.1	1.5	3.8	260	2.8-0.8	13.5	10.5	70.0	2
18/3/93	5.93	0.1	3.1	1.8	0.8	2.7	0.6	13.8	2.5	2.7	3.8	12.5	260	2.9-0.8	13.5	10.5	70.0	2
15/4/93	49.73	23.9	41.3	No Reading	No Reading	3.7	No Reading	No Reading	3.3	3.1	1.9	13.6	220	5.2-3.4	14.0	10.5	65.0	2
18/4/93	25.53	15.7	42.7	No Reading	No Reading	2.1	No Reading	No Reading	4.6	13.3	20.0	10.1	320	3.2-1.2	15.0	12.0	70.0	2
24/4/93	69.43	23.1	34.7	No Reading	No Reading	89.3	No Reading	No Reading	45.3	100.9	32.3	48.5	90	0.2-1.6	9.5	5.0	50.0	2
29/4/93	6.53	10.2	42.7	No Reading	No Reading	2.3	No Reading	No Reading	3.5	8.9	10.1	54.9	40	2-1.3	15.5	13.5	80.0	0
Min	0.9	0.0	0.0	0.7	0.0	0.3	0.4	4.8	0.0	2.7	0.7	1.7	28.0	0.0	0.0	0.5	50.0	
Max	76.5	57.9	77.8	21.6	34.1	127.6	36.4	64.1	68.0	160.9	59.2	156.7	340.0	16.5	25.5	75.0	100.0	
Average	19.0	7.2	20.9	5.4	5.4	17.7	9.0	14.8	14.1	30.2	10.3	29.5	191.2	5.5	13.0	11.7	75.8	
Stdev	14.9	12.1	18.9	5.7	7.5	21.6	8.3	11.3	16.6	31.7	11.3	27.1	94.0	9.5	6.0	10.1	12.2	

Appendix B (ii)

The lead isotopic ratios and concentrations of all the soils, rain, tap water, seawater and petrol sources tested during this study.

The Pb isotopic ratios and concentrations of Milton Keynes rain.

Sample	Date	$^{207}Pb/^{206}Pb$	Error	$^{204}Pb/^{207}Pb$	Error	$^{208}Pb/^{207}Pb$	Error	Pb Conc (ng/ml)	Error
Rain	25/3/93	0.81042	2.8E-04	0.06456	5.1E-05	2.38975	5.6E-04	5.06	0.08
Rain	30/4/93	0.10675	7.1E-05	0.06442	2.9E-04	2.37571	9.5E-04	0.03	0.01
Rain	14/5/93	0.72851	2.3E-04	0.06574	1.9E-04	2.38601	9.0E-04	3.79	0.76
Rain	18/6/93	0.80227	1.1E-03	0.06422	9.8E-05	2.39453	3.9E-03	13.00	0.70
Rain	1/7/93	0.90321	3.4E-04	0.06468	1.6E-04	2.38629	3.1E-03	2.53	0.40
Rain	18/8/93	0.07965	2.9E-04	0.06494	6.2E-05	2.37962	5.6E-04	5.06	0.80
Max		**0.90321**	**1.1E-03**	**0.06574**	**2.9E-04**	**2.39453**	**3.9E-03**	**13.00**	**0.80**
Min		**0.07965**	**7.1E-05**	**0.06422**	**5.1E-05**	**2.37571**	**5.6E-04**	**0.03**	**0.01**
Mean		**0.57180**	**3.8E-04**	**0.06476**	**1.4E-04**	**2.38532**	**1.7E-03**	**4.91**	**0.46**
Stdev		**0.37495**	**3.5E-04**	**0.00054**	**9.2E-05**	**0.00679**	**1.4E-03**	**4.39**	**0.35**

The Pb isotopic ratios and concentrations of Milton Keynes tap water

Sample	$^{207}Pb/^{206}Pb$	Error	$^{204}Pb/^{207}Pb$	Error	$^{208}Pb/^{207}Pb$	Error	Pb Conc (ng/ml)	Error
Tap water	0.24134	6.4E-05	0.06450	1.2E-04	2.41112	8.9E-04	4.84	0.002
Tap Water	0.73293	1.8E-04	0.06456	3.2E-05	2.41271	6.6E-04	39.89	0.001
Max	**0.73293**	**1.8E-04**	**0.06456**	**1.2E-04**	**2.41271**	**8.9E-04**	**39.89**	**0.002**
Min	**0.24134**	**6.4E-05**	**0.06450**	**3.2E-05**	**2.41112**	**6.6E-04**	**4.84**	**0.001**
Mean	**0.48713**	**1.2E-04**	**0.06453**	**7.4E-05**	**2.41191**	**7.8E-04**	**22.36**	**0.001**
Stdev	**0.34760**	**8.3E-05**	**0.00005**	**5.9E-05**	**0.00113**	**1.6E-04**	**24.79**	**0.001**

Appendix B (ii)

(continued)

The lead isotopic ratios and concentrations of all the soils, rain, tap water, seawater and petrol sources tested during this study.

The Pb isotopic ratios and concentartions of Swansea seawater.

Sample	$^{207}Pb/^{206}Pb$	Error	$^{204}Pb/^{207}Pb$	Error	$^{208}Pb/^{207}Pb$	Error	Pb Conc (ng/ml)	Error
Swansea seawater	0.25319	7.3E-05	0.06408	1.2E-04	2.40212	9.8E-04	23.50	0.002
Swansea seawater	0.15351	1.8E-04	0.06568	9.1E-04	2.39335	4.1E-03	6.30	0.002
Swansea seawater	0.24389	9.2E-05	0.06394	1.7E-04	2.40915	1.9E-03	11.00	0.003
Max	**0.25319**	**1.8E-04**	**0.06568**	**9.1E-04**	**2.40915**	**4.1E-03**	**23.50**	**0.003**
Min	**0.15351**	**7.3E-05**	**0.06394**	**1.2E-04**	**2.39335**	**9.8E-04**	**6.30**	**0.002**
Mean	**0.21686**	**1.1E-04**	**0.06456**	**4.0E-04**	**2.40154**	**2.3E-03**	**13.60**	**0.002**
Stdev	**0.05506**	**5.6E-05**	**0.00097**	**4.4E-04**	**0.00791**	**1.6E-03**	**8.89**	**0.001**

The Pb isotopic ratios and concentartions of Broadhaven seawater.

Sample	$^{207}Pb/^{206}Pb$	Error	$^{204}Pb/^{207}Pb$	Error	$^{208}Pb/^{207}Pb$	Error	Pb Conc (ng/ml)	Error
Broadhaven seawater	0.21197	6.0E-05	0.06379	1.6E-04	2.40838	7.4E-04	9.40	0.002
Broadhaven seawater	0.15995	6.8E-05	0.06398	2.7E-04	2.39729	1.0E-03	128.00	0.001
Broadhaven seawater	0.09949	2.3E-05	0.06483	3.4E-04	2.38012	1.7E-03	3.70	0.007
Broadhaven seawater	0.15700	8.6E-05	0.06458	2.4E-04	2.35057	1.7E-03	5.70	0.001
Max	**0.21197**	**8.6E-05**	**0.06483**	**3.4E-04**	**2.40838**	**1.7E-03**	**128.00**	**0.007**
Min	**0.09949**	**2.3E-05**	**0.06379**	**1.6E-04**	**2.35057**	**7.4E-04**	**3.70**	**0.001**
Mean	**0.15710**	**5.9E-05**	**0.06429**	**2.5E-04**	**2.38409**	**1.3E-03**	**36.70**	**0.003**
Stdev	**0.04596**	**2.7E-05**	**0.00049**	**7.5E-05**	**0.02519**	**4.8E-04**	**60.91**	**0.003**

Appendix B (ii)

(continued)

The lead isotopic ratios and concentrations of all the soils, rain, tap water, seawater and petrol sources tested during this study.

The Pb isotopic ratios and concentrations of Broadhaven soil.

Sample	$^{207}Pb/^{206}Pb$	Error	$^{204}Pb/^{207}Pb$	Error	$^{208}Pb/^{207}Pb$	Error	Pb Conc (ng/ml)	Error
Broadhaven soil	0.84800	6.2E-04	0.06422	7.1E-04	2.43995	2.1E-03	0.63	0.01
Broadhaven soil	0.84678	5.6E-04	0.06456	5.0E-05	2.43861	5.6E-04	0.42	0.04
Max	**0.84800**	**6.2E-04**	**0.06456**	**7.1E-04**	**2.43995**	**2.1E-03**	**0.63**	**0.040**
Min	**0.84678**	**5.6E-04**	**0.06422**	**5.0E-05**	**2.43861**	**5.6E-04**	**0.42**	**0.005**
Mean	**0.84739**	**5.9E-04**	**0.06439**	**3.8E-04**	**2.43928**	**1.3E-03**	**0.53**	**0.023**
Stdev	**0.00086**	**4.2E-05**	**0.00024**	**4.7E-04**	**0.00095**	**1.1E-03**	**0.15**	**0.024**

The Pb isotopic ratios and concentrations of Mean Llea soil.

Sample	$^{207}Pb/^{206}Pb$	Error	$^{204}Pb/^{207}Pb$	Error	$^{208}Pb/^{207}Pb$	Error	Pb Conc (ng/ml)	Error
Mean Llea soil	0.08463	6.2E-04	0.06438	6.2E-05	2.44862	5.2E-04	0.68	0.07
Mean Llea soil	0.84567	3.4E-04	0.06433	5.6E-05	2.44863	6.2E-05	0.23	0.03
Mean Llea soil	0.84342	1.8E-04	0.06432	2.3E-05	2.44220	5.0E-04	4.62	0.21
Mean Llea soil	0.84298	1.7E-04	0.06430	1.3E-05	2.44203	5.3E-04	7.00	0.15
Max	**0.84567**	**6.2E-04**	**0.06438**	**6.2E-05**	**2.44863**	**5.3E-04**	**7.00**	**0.21**
Min	**0.08463**	**1.7E-04**	**0.06430**	**1.3E-05**	**2.44203**	**6.2E-05**	**0.23**	**0.03**
Mean	**0.65418**	**3.3E-04**	**0.06433**	**3.9E-05**	**2.44537**	**4.0E-04**	**3.13**	**0.12**
Stdev	**0.37970**	**2.1E-04**	**0.00004**	**2.4E-05**	**0.00376**	**2.3E-04**	**3.25**	**0.08**

The Pb isotopic ratios and concentrations of Milton Keynes soil.

Sample	$^{207}Pb/^{206}Pb$	Error	$^{204}Pb/^{207}Pb$	Error	$^{208}Pb/^{207}Pb$	Error	Pb Conc (ng/ml)	Error
Milton Keynes soil	0.83621	3.4E-04	0.06412	6.7E-05	2.46528	6.2E-04	0.29	0.04
Milton Keynes soil	0.83355	1.9E-04	0.06403	1.7E-05	2.46105	3.0E-05	0.17	0.18
Milton Keynes soil	0.83333	1.5E-04	0.06411	1.6E-05	2.46262	1.6E-04	8.21	0.80
Max	**0.83621**	**3.4E-04**	**0.06412**	**6.7E-05**	**2.46528**	**6.2E-04**	**8.21**	**0.80**
Min	**0.83333**	**1.5E-04**	**0.06403**	**1.6E-05**	**2.46105**	**3.0E-05**	**0.17**	**0.04**
Mean	**0.83436**	**2.3E-04**	**0.06409**	**3.3E-05**	**2.46298**	**2.7E-04**	**2.89**	**0.34**
Stdev	**0.00160**	**1.0E-04**	**0.00005**	**2.9E-05**	**0.00214**	**3.1E-04**	**4.61**	**0.40**

Appendix B (iii)

Milton Keynes data correlation coefficients for carbon and lead concentration, $\delta^{13}C$, $^{204}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratio data.

	Carbon conc	$\delta^{13}C$	$^{204}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Lead conc
Carbon conc	1.000	-0.291	-0.245	-0.144	-0.118
$\delta^{13}C$	-0.291	1.000	0.124	0.475	-0.127
$^{204}Pb/^{207}Pb$	-0.245	0.124	1.000	-0.068	0.038
$^{208}Pb/^{207}Pb$	-0.144	0.475	-0.068	1.000	0.009
Lead conc	-0.118	-0.127	0.038	0.009	1.000

Factor Analysis Summary

Number of Variables	7
Est. Number of Factors	3
Number of Factors	3
Number of Cases	112
Number Missing	7
Degrees of Freedom	27
Bartlett's Chi Square	60.901
P-Value	.0002

Factor Extraction Method: Principal Components
Extraction Rule: Method Default
Transformation Method: Orthotran/Varimax

Unrotated Factors

	Factor 1	Factor 2	Factor 3
Rain	-.407	-.352	-.260
Pb Conc	.388	.513	.059
204Pb/207Pb	.230	.073	.753
208Pb/207Pb	.607	-.221	-.492
C Conc	-.639	.249	-.321
d13 C	.790	-.046	-.276
Wind Dir	-.035	.823	-.265

Correlation Matrix

	C Conc	d13 C	204Pb/207Pb	208Pb/207Pb	Rain	Pb Conc
C Conc	1.000	-.319	-.153	-.175	.057	-.244
d13 C	-.319	1.000	.012	.439	-.194	.129
204Pb/207Pb	-.153	.012	1.000	-.019	-.142	.035
208Pb/207Pb	-.175	.439	-.019	1.000	2.036E-3	.061
Rain	.057	-.194	-.142	2.036E-3	1.000	-.076
Pb Conc	-.244	.129	.035	.061	-.076	1.000

Proportionate Variance Contributions

	Orthogonal - Direct	Oblique - Direct	Oblique - Joint	Oblique - Total
Factor 1	.458	.284	.119	.403
Factor 2	.299	.186	.072	.258
Factor 3	.243	.153	.186	.340

Wales 1992 factor analysis data.

Factor Analysis Summary

Number of Variables	5
Est. Number of Factors	2
Number of Factors	2
Number of Cases	25
Number Missing	0
Degrees of Freedom	14
Bartlett's Chi Square	35.312
P-Value	.0013

Factor Extraction Method: Principal Components
Extraction Rule: Method Default
Transformation Method: Orthotran/Varimax

Unrotated Factors

	Factor 1	Factor 2
208Pb/207Pb	-.466	.707
204Pb/207Pb	.642	.584
Pb Concentration	.800	-.073
d13C	-.750	-.502
C Concentration	-.531	.685

Correlation Matrix

	208Pb/207Pb	204Pb/207Pb	Pb Concentration	d13C	C Concentration
208Pb/207Pb	1.000	.072	-.280	.070	.545
204Pb/207Pb	.072	1.000	.309	-.646	-.032
Pb Concentration	-.280	.309	1.000	-.478	-.386
d13C	.070	-.646	-.478	1.000	.012
C Concentration	.545	-.032	-.386	.012	1.000

Proportionate Variance Contributions

	Orthogonal - Direct	Oblique - Direct	Oblique - Joint	Oblique - Total
Factor 1	.384	.410	-.077	.332
Factor 2	.298	.320	-6.585E-3	.314
Factor 3	.318	.337	.017	.354

Wales 1993 factor analysis data.

Factor Analysis Summary

Number of Variables	6
Est. Number of Factors	3
Number of Factors	3
Number of Cases	40
Number Missing	0
Degrees of Freedom	20
Bartlett's Chi Square	66.038
P-Value	<.0001

Factor Extraction Method: Principal Components
Extraction Rule: Method Default
Transformation Method: Orthotran/Varimax

Unrotated Factors

	Factor 1	Factor 2	Factor 3
204Pb/207Pb	.934	-.141	-.088
208Pb/207Pb	.704	-.023	.112
Pb Conc	.147	.156	.904
13/12C	-.701	.556	.102
C concentration (g/m3)	.325	.699	-.425
Wind dir	.507	.567	.159

Proportionate Variance Contributions

	Orthogonal - Direct	Oblique - Direct	Oblique - Joint	Oblique - Total
Factor 1	.523	.509	-8.476E-3	.501
Factor 2	.477	.464	.035	.499

Appendix B(iv)

Milton Keynes t-test results.

t-Test: Two-Sample Assuming Unequal Variances

	C concentration	C concentration
Mean	36.11	23.84
Variance	136.79	117.86
Observations	37	26
Pooled Variance	3.5	
df	56.36	
t	4.27	
P(T<=t) two-tail	7.47E-05	
t Critical two-tail	2.00	

t-Test: Two-Sample Assuming Unequal Variances

	$\delta^{13}C$	$\delta^{13}C$
Mean	-19.09	-17.32
Variance	9.76	18.13
Observations	37	26
Pooled Variance	3.5	
df	43.19	
t	-1.80	
P(T<=t) two-tail	0.07	
t Critical two-tail	2.01	

t-Test: Two-Sample Assuming Unequal Variances

	$^{204}Pb/^{207}Pb$	$^{204}Pb/^{207}Pb$
Mean	0.064	0.064
Variance	1.1311E-06	2.8723E-07
Observations	37	26

Pooled Variance	3.5
df	56.15
t	-0.36
P(T<=t) two-tail	0.71
t Critical two-tail	2.00

t-Test: Two-Sample Assuming Unequal Variances

	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Mean	2.37	2.38
Variance	8.7036E-05	0.001
Observations	37	26
Pooled Variance	3.5	
df	43.67	
t	-3.02	
P(T<=t) two-tail	0.004	
t Critical two-tail	2.016	

Appendix B (v)

Mixing model 1.
The results of a Pb isotope mixing model of Milton keynes regolith and petrol-derived particles.

$^{208}Pb/^{207}Pb$ Milton Keynes regolith	$^{204}Pb/^{207}Pb$ Milton Keynes regolith	F1	$^{208}Pb/^{207}Pb$ Petrol	$^{204}Pb/^{207}Pb$ Petrol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.463	0.0641	1	2.326	0.0654	1	0.0641	2.463
2.463	0.0641	0.9	2.326	0.0654	0.9	0.06423	2.449
2.463	0.0641	0.8	2.326	0.0654	0.8	0.06436	2.435
2.463	0.0641	0.7	2.326	0.0654	0.7	0.06449	2.421
2.463	0.0641	0.6	2.326	0.0654	0.6	0.06462	2.408
2.463	0.0641	0.5	2.326	0.0654	0.5	0.06475	2.394
2.463	0.0641	0.4	2.326	0.0654	0.4	0.06488	2.380
2.463	0.0641	0.3	2.326	0.0654	0.3	0.06501	2.367
2.463	0.0641	0.2	2.326	0.0654	0.2	0.06514	2.353
2.463	0.0641	0.1	2.326	0.0654	0.1	0.06527	2.339
2.463	0.0641	0	2.326	0.0654	0	0.0654	2.326

Mixing model 2a.

The results of a Pb isotope mixing model of unknown industrial X and Broadhaven seawater-derived particles.

$^{208}Pb/^{207}Pb$ Broadhaven seawater	$^{204}Pb/^{207}Pb$ Broadhaven seawater	F1	$^{208}Pb/^{207}Pb$ Unknown X	$^{204}Pb/^{207}Pb$ Unknown X	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.394	0.0638	1	2.45	0.0665	1	0.0638	2.394
2.394	0.0638	0.9	2.45	0.0665	0.9	0.06407	2.400
2.394	0.0638	0.8	2.45	0.0665	0.8	0.06434	2.406
2.394	0.0638	0.7	2.45	0.0665	0.7	0.06461	2.411
2.394	0.0638	0.6	2.45	0.0665	0.6	0.06488	2.417
2.394	0.0638	0.5	2.45	0.0665	0.5	0.06515	2.423
2.394	0.0638	0.4	2.45	0.0665	0.4	0.06542	2.428
2.394	0.0638	0.3	2.45	0.0665	0.3	0.06569	2.434
2.394	0.0638	0.2	2.45	0.0665	0.2	0.06596	2.439
2.394	0.0638	0.1	2.45	0.0665	0.1	0.06623	2.445
2.394	0.0638	0	2.45	0.0665	0	0.0665	2.450

Mixing model 2b.

The results of a Pb isotope mixing model of unknown industrial Y and Broadhaven seawater-derived particles.

$^{208}Pb/^{207}Pb$ Unknown Y	$^{204}Pb/^{207}Pb$ Unknown Y	F1	$^{208}Pb/^{207}Pb$ Broadhaven seawater	$^{204}Pb/^{207}Pb$ Broadhaven seawater	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.425	0.0641	1	2.394	0.0638	1	0.0641	2.425
2.425	0.0641	0.9	2.394	0.0638	0.9	0.0641	2.422
2.425	0.0641	0.8	2.394	0.0638	0.8	0.0640	2.419
2.425	0.0641	0.7	2.394	0.0638	0.7	0.0640	2.416
2.425	0.0641	0.6	2.394	0.0638	0.6	0.0640	2.413
2.425	0.0641	0.5	2.394	0.0638	0.5	0.0640	2.410
2.425	0.0641	0.4	2.394	0.0638	0.4	0.0639	2.406
2.425	0.0641	0.3	2.394	0.0638	0.3	0.0639	2.403
2.425	0.0641	0.2	2.394	0.0638	0.2	0.0639	2.400
2.425	0.0641	0.1	2.394	0.0638	0.1	0.0638	2.397
2.425	0.0641	0	2.394	0.0638	0	0.0638	2.394

Mixing model 2c.
The results of a Pb isotope mixing model of unknown industrial X and Swansea seawater-derived particles.

$^{208}Pb/^{207}Pb$ Unknown X	$^{204}Pb/^{207}Pb$ Unknown X	F1	$^{208}Pb/^{207}Pb$ Swansea seawater	$^{204}Pb/^{207}Pb$ swansea seawater	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.45	0.0665	1	2.413	0.06638	1	0.0665	2.450
2.45	0.0665	0.9	2.413	0.06638	0.9	0.0665	2.446
2.45	0.0665	0.8	2.413	0.06638	0.8	0.0665	2.443
2.45	0.0665	0.7	2.413	0.06638	0.7	0.0665	2.439
2.45	0.0665	0.6	2.413	0.06638	0.6	0.0665	2.435
2.45	0.0665	0.5	2.413	0.06638	0.5	0.0664	2.432
2.45	0.0665	0.4	2.413	0.06638	0.4	0.0664	2.428
2.45	0.0665	0.3	2.413	0.06638	0.3	0.0664	2.424
2.45	0.0665	0.2	2.413	0.06638	0.2	0.0664	2.420
2.45	0.0665	0.1	2.413	0.06638	0.1	0.0664	2.417
2.45	0.0665	0	2.413	0.06638	0	0.0664	2.413

Mixing model 2d.
The results of a Pb isotope mixing model of unknown industrial Y and Swansea seawater-derived particles.

$^{208}Pb/^{207}Pb$ Unknown Y	$^{204}Pb/^{207}Pb$ Unknown Y	F1	$^{208}Pb/^{207}Pb$ Swansea seawater	$^{204}Pb/^{207}Pb$ Swansea seawater	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.425	0.0641	1	2.413	0.06638	1	0.0641	2.425
2.425	0.0641	0.9	2.413	0.06638	0.9	0.0643	2.424
2.425	0.0641	0.8	2.413	0.06638	0.8	0.0646	2.423
2.425	0.0641	0.7	2.413	0.06638	0.7	0.0648	2.421
2.425	0.0641	0.6	2.413	0.06638	0.6	0.0650	2.420
2.425	0.0641	0.5	2.413	0.06638	0.5	0.0652	2.419
2.425	0.0641	0.4	2.413	0.06638	0.4	0.0655	2.418
2.425	0.0641	0.3	2.413	0.06638	0.3	0.0657	2.417
2.425	0.0641	0.2	2.413	0.06638	0.2	0.0659	2.415
2.425	0.0641	0.1	2.413	0.06638	0.1	0.0662	2.414
2.425	0.0641	0	2.413	0.06638	0	0.0664	2.413

Mixing model 2e.

The results of a Pb isotope mixing model of unknown industrial X and mean Rhoscrowther aerosol value.

$^{208}Pb/^{207}Pb$ Unknown X	$^{204}Pb/^{207}Pb$ Unknown X	F1	$^{208}Pb/^{207}Pb$ Mean Rhoscrowther aerosol	$^{204}Pb/^{207}Pb$ Mean Rhoscrowther aerosol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.45	0.0665	1	2.415	0.0639	1	0.0665	2.450
2.45	0.0665	0.9	2.415	0.0639	0.9	0.0662	2.447
2.45	0.0665	0.8	2.415	0.0639	0.8	0.0660	2.443
2.45	0.0665	0.7	2.415	0.0639	0.7	0.0657	2.440
2.45	0.0665	0.6	2.415	0.0639	0.6	0.0655	2.436
2.45	0.0665	0.5	2.415	0.0639	0.5	0.0652	2.433
2.45	0.0665	0.4	2.415	0.0639	0.4	0.0649	2.429
2.45	0.0665	0.3	2.415	0.0639	0.3	0.0647	2.426
2.45	0.0665	0.2	2.415	0.0639	0.2	0.0644	2.422
2.45	0.0665	0.1	2.415	0.0639	0.1	0.0642	2.419
2.45	0.0665	0	2.415	0.0639	0	0.0639	2.415

Mixing model 2f.

The results of a Pb isotope mixing model of unknown industrial Y and mean Rhoscrowther aerosol value.

$^{208}Pb/^{207}Pb$ Unknown Y	$^{204}Pb/^{207}Pb$ Unknown Y	F1	$^{208}Pb/^{207}Pb$ Mean Rhoscrowther aerosol	$^{204}Pb/^{207}Pb$ Mean Rhoscrowther aerosol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.425	0.0641	1	2.415	0.0639	1	0.0641	2.425
2.425	0.0641	0.9	2.415	0.0639	0.9	0.0641	2.424
2.425	0.0641	0.8	2.415	0.0639	0.8	0.0641	2.423
2.425	0.0641	0.7	2.415	0.0639	0.7	0.0640	2.422
2.425	0.0641	0.6	2.415	0.0639	0.6	0.0640	2.421
2.425	0.0641	0.5	2.415	0.0639	0.5	0.0640	2.420
2.425	0.0641	0.4	2.415	0.0639	0.4	0.0640	2.419
2.425	0.0641	0.3	2.415	0.0639	0.3	0.0640	2.418
2.425	0.0641	0.2	2.415	0.0639	0.2	0.0639	2.417
2.425	0.0641	0.1	2.415	0.0639	0.1	0.0639	2.416
2.425	0.0641	0	2.415	0.0639	0	0.0639	2.415

Mixing model 2g.

The results of a Pb isotope mixing model of unknown Z and mean Rhoscrowther aerosol value.

$^{208}Pb/^{207}Pb$ Unknown Z	$^{204}Pb/^{207}Pb$ Unknown Z	F1	$^{208}Pb/^{207}Pb$ Mean Rhoscrowther aerosol	$^{204}Pb/^{207}Pb$ Mean Rhoscrowther aerosol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.34	0.0634	1	2.415	0.0639	1	0.0634	2.340
2.34	0.0634	0.9	2.415	0.0639	0.9	0.0635	2.348
2.34	0.0634	0.8	2.415	0.0639	0.8	0.0635	2.355
2.34	0.0634	0.7	2.415	0.0639	0.7	0.0636	2.363
2.34	0.0634	0.6	2.415	0.0639	0.6	0.0636	2.370
2.34	0.0634	0.5	2.415	0.0639	0.5	0.0637	2.378
2.34	0.0634	0.4	2.415	0.0639	0.4	0.0637	2.385
2.34	0.0634	0.3	2.415	0.0639	0.3	0.0638	2.393
2.34	0.0634	0.2	2.415	0.0639	0.2	0.0638	2.400
2.34	0.0634	0.1	2.415	0.0639	0.1	0.0639	2.408
2.34	0.0634	0	2.415	0.0639	0	0.0639	2.415

Mixing model 2h.

The results of a Pb isotope mixing model of unknown X and mean Port Talbot aerosol value.

$^{208}Pb/^{207}Pb$ Unknown X	$^{204}Pb/^{207}Pb$ Unknown X	F1	$^{208}Pb/^{207}Pb$ Mean Port Talbot aerosol	$^{204}Pb/^{207}Pb$ Mean Port Talbot aerosol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.45	0.0665	1	2.413	0.06638	1	0.0665	2.450
2.45	0.0665	0.9	2.413	0.06638	0.9	0.0665	2.446
2.45	0.0665	0.8	2.413	0.06638	0.8	0.0665	2.443
2.45	0.0665	0.7	2.413	0.06638	0.7	0.0665	2.439
2.45	0.0665	0.6	2.413	0.06638	0.6	0.0665	2.435
2.45	0.0665	0.5	2.413	0.06638	0.5	0.0664	2.432
2.45	0.0665	0.4	2.413	0.06638	0.4	0.0664	2.428
2.45	0.0665	0.3	2.413	0.06638	0.3	0.0664	2.424
2.45	0.0665	0.2	2.413	0.06638	0.2	0.0664	2.420
2.45	0.0665	0.1	2.413	0.06638	0.1	0.0664	2.417
2.45	0.0665	0	2.413	0.06638	0	0.0664	2.413

Mixing model 2i.

The results of a Pb isotope mixing model of unknown Y and mean Port Talbot aerosol value.

$^{208}Pb/^{207}Pb$ Unknown Y	$^{204}Pb/^{207}Pb$ Unknown Y	F1	$^{208}Pb/^{207}Pb$ Mean Port Talbot aerosol	$^{204}Pb/^{207}Pb$ Mean Port Talbot aerosol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.425	0.0641	1	2.413	0.06638	1	0.0641	2.425
2.425	0.0641	0.9	2.413	0.06638	0.9	0.0643	2.424
2.425	0.0641	0.8	2.413	0.06638	0.8	0.0646	2.423
2.425	0.0641	0.7	2.413	0.06638	0.7	0.0648	2.421
2.425	0.0641	0.6	2.413	0.06638	0.6	0.0650	2.420
2.425	0.0641	0.5	2.413	0.06638	0.5	0.0652	2.419
2.425	0.0641	0.4	2.413	0.06638	0.4	0.0655	2.418
2.425	0.0641	0.3	2.413	0.06638	0.3	0.0657	2.417
2.425	0.0641	0.2	2.413	0.06638	0.2	0.0659	2.415
2.425	0.0641	0.1	2.413	0.06638	0.1	0.0662	2.414
2.425	0.0641	0	2.413	0.06638	0	0.0664	2.413

Mixing model 2j.

The results of a Pb isotope mixing model of unknown Z and mean Port Talbot aerosol value.

$^{208}Pb/^{207}Pb$ Unknown Z	$^{204}Pb/^{207}Pb$ Unknown Z	F1	$^{208}Pb/^{207}Pb$ Mean Port Talbot aerosol	$^{204}Pb/^{207}Pb$ Mean Port Talbot aerosol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.34	0.0634	1	2.413	0.06638	1	0.0634	2.340
2.34	0.0634	0.9	2.413	0.06638	0.9	0.0637	2.348
2.34	0.0634	0.8	2.413	0.06638	0.8	0.0640	2.355
2.34	0.0634	0.7	2.413	0.06638	0.7	0.0643	2.363
2.34	0.0634	0.6	2.413	0.06638	0.6	0.0646	2.370
2.34	0.0634	0.5	2.413	0.06638	0.5	0.0649	2.377
2.34	0.0634	0.4	2.413	0.06638	0.4	0.0652	2.385
2.34	0.0634	0.3	2.413	0.06638	0.3	0.0655	2.392
2.34	0.0634	0.2	2.413	0.06638	0.2	0.0658	2.399
2.34	0.0634	0.1	2.413	0.06638	0.1	0.0661	2.406
2.34	0.0634	0	2.413	0.06638	0	0.0664	2.413

Mixing model 3a.

The results of a Pb isotope mixing model of unknown industrial component Y and petrol -derived particles.

$^{208}Pb/^{207}Pb$ Unknown Y	$^{204}Pb/^{207}Pb$ Unknown Y	F1	$^{208}Pb/^{207}Pb$ Petrol	$^{204}Pb/^{207}Pb$ Petrol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.425	0.0641	1	2.326	0.0654	1	0.0641	2.425
2.425	0.0641	0.9	2.326	0.0654	0.9	0.0642	2.415
2.425	0.0641	0.8	2.326	0.0654	0.8	0.0644	2.405
2.425	0.0641	0.7	2.326	0.0654	0.7	0.0645	2.395
2.425	0.0641	0.6	2.326	0.0654	0.6	0.0646	2.385
2.425	0.0641	0.5	2.326	0.0654	0.5	0.0648	2.375
2.425	0.0641	0.4	2.326	0.0654	0.4	0.0649	2.365
2.425	0.0641	0.3	2.326	0.0654	0.3	0.0650	2.355
2.425	0.0641	0.2	2.326	0.0654	0.2	0.0651	2.345
2.425	0.0641	0.1	2.326	0.0654	0.1	0.0653	2.336
2.425	0.0641	0	2.326	0.0654	0	0.0654	2.326

Mixing model 3b.

The results of a Pb isotope mixing model of unknown industrial component Z and petrol -derived particles.

$^{208}Pb/^{207}Pb$ Unknown Z	$^{204}Pb/^{207}Pb$ Unknown Z	F1	$^{208}Pb/^{207}Pb$ Petrol	$^{204}Pb/^{207}Pb$ Petrol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.34	0.0634	1	2.326	0.0654	1	0.0634	2.340
2.34	0.0634	0.9	2.326	0.0654	0.9	0.0636	2.339
2.34	0.0634	0.8	2.326	0.0654	0.8	0.0638	2.337
2.34	0.0634	0.7	2.326	0.0654	0.7	0.0640	2.336
2.34	0.0634	0.6	2.326	0.0654	0.6	0.0642	2.334
2.34	0.0634	0.5	2.326	0.0654	0.5	0.0644	2.333
2.34	0.0634	0.4	2.326	0.0654	0.4	0.0646	2.331
2.34	0.0634	0.3	2.326	0.0654	0.3	0.0648	2.330
2.34	0.0634	0.2	2.326	0.0654	0.2	0.0650	2.329
2.34	0.0634	0.1	2.326	0.0654	0.1	0.0652	2.327
2.34	0.0634	0	2.326	0.0654	0	0.0654	2.326

Mixing model 3c.

The results of a Pb isotope mixing model of unknown industrial component X and unknown component Z -derived particles.

$^{208}Pb/^{207}Pb$ Unknown X	$^{204}Pb/^{207}Pb$ Unknown X	F1	$^{208}Pb/^{207}Pb$ Unknown Z	$^{204}Pb/^{207}Pb$ Unknown Z	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.45	0.0665	1	2.34	0.0634	1	0.0665	2.450
2.45	0.0665	0.9	2.34	0.0634	0.9	0.0662	2.439
2.45	0.0665	0.8	2.34	0.0634	0.8	0.0659	2.429
2.45	0.0665	0.7	2.34	0.0634	0.7	0.0656	2.418
2.45	0.0665	0.6	2.34	0.0634	0.6	0.0653	2.407
2.45	0.0665	0.5	2.34	0.0634	0.5	0.0650	2.396
2.45	0.0665	0.4	2.34	0.0634	0.4	0.0646	2.385
2.45	0.0665	0.3	2.34	0.0634	0.3	0.0643	2.374
2.45	0.0665	0.2	2.34	0.0634	0.2	0.0640	2.363
2.45	0.0665	0.1	2.34	0.0634	0.1	0.0637	2.351
2.45	0.0665	0	2.34	0.0634	0	0.0634	2.340

Mixing model 3d.

The results of a Pb isotope mixing model of unknown industrial component Y and unknown component Z -derived particles.

$^{208}Pb/^{207}Pb$ Unknown Unknown Y	$^{204}Pb/^{207}Pb$ Unknown Unknown Y	F1	$^{208}Pb/^{207}Pb$ Unknown Unknown Z	$^{204}Pb/^{207}Pb$ Unknown Unknown Z	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.425	0.0641	1	2.34	0.0634	1	0.0641	2.425
2.425	0.0641	0.9	2.34	0.0634	0.9	0.0640	2.417
2.425	0.0641	0.8	2.34	0.0634	0.8	0.0640	2.408
2.425	0.0641	0.7	2.34	0.0634	0.7	0.0639	2.400
2.425	0.0641	0.6	2.34	0.0634	0.6	0.0638	2.391
2.425	0.0641	0.5	2.34	0.0634	0.5	0.0638	2.383
2.425	0.0641	0.4	2.34	0.0634	0.4	0.0637	2.374
2.425	0.0641	0.3	2.34	0.0634	0.3	0.0636	2.366
2.425	0.0641	0.2	2.34	0.0634	0.2	0.0635	2.357
2.425	0.0641	0.1	2.34	0.0634	0.1	0.0635	2.349
2.425	0.0641	0	2.34	0.0634	0	0.0634	2.340

Mixing model 4a.

The results of a Pb isotope mixing model of Broadhaven seawater and petrol-derived particles.

$^{208}Pb/^{207}Pb$ Broadhaven Seawater	$^{204}Pb/^{207}Pb$ Broadhaven Seawater	F1	$^{208}Pb/^{207}Pb$ Petrol	$^{204}Pb/^{207}Pb$ Petrol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.393	0.0638	1	2.326	0.0654	1	0.0638	2.393
2.393	0.0638	0.9	2.326	0.0654	0.9	0.0639	2.387
2.393	0.0638	0.8	2.326	0.0654	0.8	0.0641	2.38
2.393	0.0638	0.7	2.326	0.0654	0.7	0.0642	2.373
2.393	0.0638	0.6	2.326	0.0654	0.6	0.0644	2.366
2.393	0.0638	0.5	2.326	0.0654	0.5	0.0646	2.359
2.393	0.0638	0.4	2.326	0.0654	0.4	0.0647	2.353
2.393	0.0638	0.3	2.326	0.0654	0.3	0.0649	2.346
2.393	0.0638	0.2	2.326	0.0654	0.2	0.0650	2.339
2.393	0.0638	0.1	2.326	0.0654	0.1	0.0652	2.333
2.393	0.0638	0	2.326	0.0654	0	0.0654	2.326

Mixing model 4b.

The results of a Pb isotope mixing model of Swansea seawater and petrol-derived particles.

$^{208}Pb/^{207}Pb$ Swansea Seawater	$^{204}Pb/^{207}Pb$ Swansea Seawater	F1	$^{208}Pb/^{207}Pb$ Petrol	$^{204}Pb/^{207}Pb$ Petrol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.402	0.064	1	2.326	0.0654	1	0.0640	2.402
2.402	0.064	0.9	2.326	0.0654	0.9	0.0641	2.394
2.402	0.064	0.8	2.326	0.0654	0.8	0.0642	2.387
2.402	0.064	0.7	2.326	0.0654	0.7	0.0644	2.379
2.402	0.064	0.6	2.326	0.0654	0.6	0.0645	2.371
2.402	0.064	0.5	2.326	0.0654	0.5	0.0647	2.364
2.402	0.064	0.4	2.326	0.0654	0.4	0.0648	2.356
2.402	0.064	0.3	2.326	0.0654	0.3	0.0649	2.348
2.402	0.064	0.2	2.326	0.0654	0.2	0.0651	2.341
2.402	0.064	0.1	2.326	0.0654	0.1	0.0652	2.333
2.402	0.064	0	2.326	0.0654	0	0.0654	2.326

Mixing model 5a.

The results of a Pb isotope mixing model of mean Mean Llea and petrol-derived particles.

$^{208}Pb/^{207}Pb$ Mean Llea soil	$^{204}Pb/^{207}Pb$ Mean Llea soil	F1	$^{208}Pb/^{207}Pb$ Petrol	$^{204}Pb/^{207}Pb$ Petrol	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.446	0.06433	1	2.326	0.0654	1	0.06433	2.446
2.446	0.06433	0.9	2.326	0.0654	0.9	0.06443	2.434
2.446	0.06433	0.8	2.326	0.0654	0.8	0.06454	2.422
2.446	0.06433	0.7	2.326	0.0654	0.7	0.06465	2.41
2.446	0.06433	0.6	2.326	0.0654	0.6	0.06475	2.398
2.446	0.06433	0.5	2.326	0.0654	0.5	0.06486	2.386
2.446	0.06433	0.4	2.326	0.0654	0.4	0.06497	2.374
2.446	0.06433	0.3	2.326	0.0654	0.3	0.06507	2.362
2.446	0.06433	0.2	2.326	0.0654	0.2	0.06518	2.35
2.446	0.06433	0.1	2.326	0.0654	0.1	0.06529	2.338
2.446	0.06433	0	2.326	0.0654	0	0.06540	2.326

Mixing model 5b.

The results of a Pb isotope mixing model of mean Rhoscrowther regolith and mean Broadhaven seawter-derived particles.

$^{208}Pb/^{207}Pb$ Mean Rhoscrowther regolith	$^{204}Pb/^{207}Pb$ Mean Rhoscrowther regolith	F1	$^{208}Pb/^{207}Pb$ Broadhaven seawater	$^{204}Pb/^{207}Pb$ Broadhaven seawater	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.469	0.0641	1	2.394	0.0638	1	0.0641	2.469
2.469	0.0641	0.9	2.394	0.0638	0.9	0.0640	2.462
2.469	0.0641	0.8	2.394	0.0638	0.8	0.0640	2.454
2.469	0.0641	0.7	2.394	0.0638	0.7	0.0640	2.447
2.469	0.0641	0.6	2.394	0.0638	0.6	0.0639	2.439
2.469	0.0641	0.5	2.394	0.0638	0.5	0.0639	2.432
2.469	0.0641	0.4	2.394	0.0638	0.4	0.0639	2.424
2.469	0.0641	0.3	2.394	0.0638	0.3	0.0638	2.417
2.469	0.0641	0.2	2.394	0.0638	0.2	0.0638	2.409
2.469	0.0641	0.1	2.394	0.0638	0.1	0.0638	2.402
2.469	0.0641	0	2.394	0.0638	0	0.0638	2.394

Mixing model 6.

The results of a Pb isotope mixing model of mean Rhoscrowther regolith and mean Rhoscrowther seawter-derived particles.

$^{208}Pb/^{207}Pb$ Mean Rhoscrowther regolith	$^{204}Pb/^{207}Pb$ Mean Rhoscrowther regolith	F1	$^{208}Pb/^{207}Pb$ Mean Rhoscrowther seawater	$^{204}Pb/^{207}Pb$ Mean Rhoscrowther seawater	F2	$^{204}Pb/^{207}Pb$ final ratio mix	$^{208}Pb/^{207}Pb$ final ratio mix
2.469	0.0641	1	2.394	0.0638	1	0.0641	2.469
2.469	0.0641	0.9	2.394	0.0638	0.9	0.06407	2.462
2.469	0.0641	0.8	2.394	0.0638	0.8	0.06404	2.454
2.469	0.0641	0.7	2.394	0.0638	0.7	0.06401	2.447
2.469	0.0641	0.6	2.394	0.0638	0.6	0.06398	2.439
2.469	0.0641	0.5	2.394	0.0638	0.5	0.06395	2.432
2.469	0.0641	0.4	2.394	0.0638	0.4	0.06392	2.424
2.469	0.0641	0.3	2.394	0.0638	0.3	0.06389	2.417
2.469	0.0641	0.2	2.394	0.0638	0.2	0.06386	2.409
2.469	0.0641	0.1	2.394	0.0638	0.1	0.06383	2.402
2.469	0.0641	0	2.394	0.0638	0	0.0638	2.394

Appendix B(vi)

(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Broadhaven site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{204}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Broadhaven	3/2/92	2.41177	1.8E-04	0.13597	2.3E-05	0.06421	1.2E-04	0.29	0.002	-19.54	0.06	66.78	0.018	9.0	6.5	75	8.4-5.4	220
Broadhaven	3/2/92	2.41077	4.3E-04	0.02045	2.5E-05	0.06562	9.4E-05	0.30	0.004	-19.54	0.06	66.78	0.036	9.0	7.0	80	8.0-5.1	220
Broadhaven	3/3/92	2.41066	1.9E-04	0.15663	2.7E-04	0.06432	5.7E-04	0.92	0.002	-18.76	0.04	41.73	0.020	9.5	9.5	100	5.8-1.9	300
Broadhaven	3/4/92	2.40863	4.3E-04	0.16215	3.0E-05	0.06601	9.1E-05	0.22	0.002	-19.79	0.05	48.79	0.020	7.5	6.0	85	7.0-2.4	220
Min		2.40863	1.8E-04	0.02045	2.3E-05	0.06421	9.1E-05	0.22	0.002	-19.79	0.04	41.73	0.018	7.5	6.0	75		220
Max		2.41177	4.3E-04	0.16215	2.7E-04	0.06601	5.7E-04	0.92	0.004	-18.76	0.06	66.78	0.036	9.5	9.5	100		300
Mean		2.41046	3.1E-04	0.11880	8.7E-05	0.06504	2.2E-04	0.43	0.002	-19.41	0.05	56.02	0.023	8.8	7.3	85		240
Stdev		0.00132	1.4E-04	0.06653	1.2E-04	0.00091	2.3E-04	0.33	0.001	0.45	0.01	12.75	0.008	0.9	1.6	11		40

Appendix B(vi)

(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Rhoscrowther site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Rhoscrowther	3/2/92	2.41777	4.3E-04	0.19558	1.6E-05	0.06592	2.5E-05	0.03	0.004	-19.73	0.10	68.57	0.036	9.5	7.5	80	0.7-0.1	300
Rhoscrowther	3/3/92	2.41666	1.2E-04	0.20598	1.8E-04	0.06451	1.9E-04	0.03	0.003	-22.64	0.01	57.94	0.024	10.5	10.0	95	5.7-0.5	220
Rhoscrowther	3/4/92	2.41729	3.1E-04	0.16667	4.2E-05	0.06743	7.3E-04	0.02	0.001	-20.35	0.06	45.17	0.009	11.5	10.0	85	1.5-0.5	220
Min		2.41666	1.2E-04	0.16667	1.6E-05	0.06451	2.5E-05	0.02	0.001	-22.64	0.01	45.17	0.009	9.5	7.5	80		220
Max		2.41777	4.3E-04	0.20598	1.8E-04	0.06743	7.3E-04	0.03	0.004	-19.73	0.10	68.57	0.036	11.5	10.0	95		300
Mean		2.41724	2.9E-04	0.18941	7.9E-05	0.06596	3.2E-04	0.03	0.002	-20.91	0.06	57.23	0.023	10.5	9.2	87		247
Stdev		0.00056	1.6E-04	0.02037	8.8E-05	0.00146	3.7E-04	0.01	0.001	1.53	0.04	11.72	0.013	1.0	1.4	8		46

Appendix B(vi)

(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for Port Talbot site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Port Talbot	2/28/92	2.37425	5.6E-04	0.40949	5.2E-05	0.06432	1.7E-04	12.10	0.6510	-20.33	0.13	30.72	0.001	9.0	6.0	73	2.6-1.3	220
Port Talbot	2/28/92	2.37262	9.7E-04	0.55603	4.4E-04	0.06421	1.1E-04	7.60	0.8310	-20.33	0.13	30.72	0.002	9.0	6.0	73	2.6-1.3	220
Port Talbot	2/29/92	2.38756	2.0E-04	0.03283	3.7E-05	0.06540	4.5E-04	6.51	0.1210	-23.64	0.08	31.79	0.078	9.0	8.0	90	2.5-1.4	60
Port Talbot	3/1/92	2.37580	1.2E-04	0.35916	2.5E-04	0.06465	5.1E-05	8.31	0.7600	-26.38	0.14	30.14	0.001	9.0	9.0	100	3.5-1.4	300
Min		2.37262	1.2E-04	0.03283	3.7E-05	0.06421	5.1E-05	6.51	0.1210	-26.38	0.08	30.14	0.001	9.0	6.0	73		60
Max		2.38756	9.7E-04	0.55603	4.4E-04	0.06540	4.5E-04	12.10	0.8310	-20.33	0.14	31.79	0.078	9.0	9.0	100		300
Mean		2.37756	4.6E-04	0.33937	1.9E-04	0.06464	2.0E-04	8.63	0.5908	-22.67	0.12	30.84	0.020	9.0	7.3	84		200
Stdev		0.00679	3.9E-04	0.22077	1.9E-04	0.00053	1.8E-04	2.43	0.3218	2.92	0.03	0.69	0.038	0.0	1.5	13		101

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(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Broadhaven site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Broadhaven	3/2/92	2.41177	1.8E-04	0.13597	2.3E-05	0.06421	1.2E-04	0.29	0.002	-19.54	0.06	66.78	0.018	9.0	6.5	75	8.4-5.4	220
Broadhaven	3/2/92	2.41077	4.3E-04	0.02045	2.5E-05	0.06562	9.4E-05	0.30	0.004	-19.54	0.06	66.78	0.036	9.0	7.0	80	8.0-5.1	220
Broadhaven	3/3/92	2.41066	1.9E-04	0.15663	2.7E-04	0.06432	5.7E-04	0.92	0.002	-18.76	0.04	41.73	0.020	9.5	9.5	100	5.8-1.9	300
Broadhaven	3/4/92	2.40863	4.3E-04	0.16215	3.0E-05	0.06601	9.1E-05	0.22	0.002	-19.79	0.05	48.79	0.020	7.5	6.0	85	7.0-2.4	220
Min		2.40863	1.8E-04	0.02045	2.3E-05	0.06421	9.1E-05	0.22	0.002	-19.79	0.04	41.73	0.018	7.5	6.0	75		220
Max		2.41177	4.3E-04	0.16215	2.7E-04	0.06601	5.7E-04	0.92	0.004	-18.76	0.06	66.78	0.036	9.5	9.5	100		300
Mean		2.41046	3.1E-04	0.11880	8.7E-05	0.06504	2.2E-04	0.43	0.002	-19.41	0.05	56.02	0.023	8.8	7.3	85		240
Stdev		0.00132	1.4E-04	0.06653	1.2E-04	0.00091	2.3E-04	0.33	0.001	0.45	0.01	12.75	0.008	0.9	1.6	11		40

Appendix B(vi)

(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Rhoscrowther site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Rhoscrowther	3/2/92	2.41777	4.3E-04	0.19558	1.6E-05	0.06592	2.5E-05	0.03	0.004	-19.73	0.10	68.57	0.036	9.5	7.5	80	0.7-0.1	300
Rhoscrowther	3/3/92	2.41666	1.2E-04	0.20598	1.8E-04	0.06451	1.9E-04	0.03	0.003	-22.64	0.01	57.94	0.024	10.5	10.0	95	5.7-0.5	220
Rhoscrowther	3/4/92	2.41729	3.1E-04	0.16667	4.2E-05	0.06743	7.3E-04	0.02	0.001	-20.35	0.06	45.17	0.009	11.5	10.0	85	1.5-0.5	220
Min		2.41666	1.2E-04	0.16667	1.6E-05	0.06451	2.5E-05	0.02	0.001	-22.64	0.01	45.17	0.009	9.5	7.5	80		220
Max		2.41777	4.3E-04	0.20598	1.8E-04	0.06743	7.3E-04	0.03	0.004	-19.73	0.10	68.57	0.036	11.5	10.0	95		300
Mean		2.41724	2.9E-04	0.18941	7.9E-05	0.06596	3.2E-04	0.03	0.002	-20.91	0.06	57.23	0.023	10.5	9.2	87		247
Stdev		0.00056	1.6E-04	0.02037	8.8E-05	0.00146	3.7E-04	0.01	0.001	1.53	0.04	11.72	0.013	1.0	1.4	8		46

Appendix B(vi)

(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for Port Talbot site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Port Talbot	2/28/92	2.37425	5.6E-04	0.40949	5.2E-05	0.06432	1.7E-04	12.10	0.6510	-20.33	0.13	30.72	0.001	9.0	6.0	73	2.6-1.3	220
Port Talbot	2/28/92	2.37262	9.7E-04	0.55603	4.4E-04	0.06421	1.1E-04	7.60	0.8310	-20.33	0.13	30.72	0.002	9.0	6.0	73	2.6-1.3	220
Port Talbot	2/29/92	2.38756	1.0E-04	0.03283	3.7E-05	0.06540	4.5E-04	6.51	0.1210	-23.64	0.08	31.79	0.078	9.0	8.0	90	2.5-1.4	60
Port Talbot	3/1/92	2.37580	1.2E-04	0.35916	2.5E-04	0.06465	5.1E-05	8.31	0.7600	-26.38	0.14	30.14	0.001	9.0	9.0	100	3.5-1.4	300
Min		2.37262	1.2E-04	0.03283	3.7E-05	0.06421	5.1E-05	6.51	0.1210	-26.38	0.08	30.14	0.001	9.0	6.0	73		60
Max		2.38756	9.7E-04	0.55603	4.4E-04	0.06540	4.5E-04	12.10	0.8310	-20.33	0.14	31.79	0.078	9.0	9.0	100		300
Mean		2.37756	4.6E-04	0.33937	1.9E-04	0.06464	2.0E-04	8.63	0.5908	-22.67	0.12	30.84	0.020	9.0	7.3	84		200
Stdev		0.00679	3.9E-04	0.22077	1.9E-04	0.00053	1.8E-04	2.43	0.3218	2.92	0.03	0.69	0.038	0.0	1.5	13		101

Appendix B(vi)

(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Swansea site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Swansea	2/27/92	2.35287	6.0E-05	0.40127	4.0E-05	0.06483	1.2E-04	1.50	0.001	-18.64	0.04	30.72	0.091	8.0	5.0	73	1.2-0.9	220
Swansea	2/27/92	2.39165	7.3E-05	0.74450	1.3E-05	0.06450	2.7E-04	13.00	3.800	-18.64	0.04	30.72	0.038	8.0	4.0	65	1.2-0.9	220
Swansea	2/28/92	2.36810	2.0E-03	0.36113	2.6E-05	0.06471	3.6E-04	0.72	0.001	-18.78	0.09	24.32	0.076	5.0	2.0	73	1.2-0.3	220
Swansea	2/28/92	2.33748	6.3E-04	0.34845	6.9E-05	0.06531	2.4E-04	0.59	0.001	-18.78	0.09	24.32	0.689	4.0	1.0	73	1.2-0.3	220
Swansea	2/29/92	2.40338	2.6E-03	0.08002	4.7E-05	0.06463	2.8E-04	0.69	0.001	-19.65	0.04	25.73	0.014	10.0	9.0	100	1.4-0.7	60
Swansea	3/1/92	2.37122	1.6E-04	0.34928	2.1E-04	0.06512	2.1E-04	0.57	0.000	-19.01	0.01	34.37	0.001	9.0	9.0	100	2.5-1.9	220
Min		2.33748	6.0E-05	0.08002	1.3E-05	0.06450	1.2E-04	0.57	0.000	-19.65	0.01	24.32	0.001	4.0	1.0	65		60
Max		2.40338	2.6E-03	0.74450	2.1E-04	0.06531	3.6E-04	13.00	3.800	-18.64	0.09	34.37	0.689	10.0	9.0	100		220
Mean		2.37078	9.2E-04	0.38077	6.8E-05	0.06485	2.5E-04	2.85	0.634	-18.92	0.05	28.36	0.151	7.3	5.0	81		193
Stdev		0.02423	1.1E-03	0.21241	7.2E-05	0.00031	8.0E-05	4.99	1.551	0.38	0.03	4.17	0.266	2.3	3.4	15		65

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(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Sarn Helen site 1992.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{206}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Erorr	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Sarn Helen	14/4/92	2.39927	6.5E-04	0.07951	1.7E-05	0.06761	2.8E-04	0.0001	0.0001	-18.71	0.08	23.46	0.083	8.0	8.0	100	5.6-3.7	60
Sarn Helen	15/4/92	2.40062	1.0E-05	0.26433	5.8E-05	0.06533	1.1E-04	0.0017	0.0001	-18.59	0.05	52.36	0.002	10.5	9.5	90	4.5-2.5	220
Sarn Helen	16/4/92	2.39827	5.1E-05	0.07480	4.5E-05	0.06669	4.0E-05	0.0002	0.0001	-19.34	0.04	47.81	0.002	8.0	6.0	70	2.8-1.1	210
Mean Llea	14/4/92	2.38857	8.5E-04	0.05737	6.4E-05	0.06513	1.0E-04	0.0001	0.0001	-18.77	0.09	49.72	0.004	8.0	7.5	95	9.2-3.5	0
Mean Llea	15/4/92	2.40102	1.9E-04	0.09643	5.0E-05	0.06578	1.3E-04	0.0002	0.0002	-19.64	0.09	63.82	0.002	10.0	9.0	90	4.0-1.9	220
Mean Llea	15/4/92	2.39194	6.7E-04	0.16592	7.0E-04	0.06618	1.6E-04	0.0002	0.0004	-19.64	0.09	63.82	0.002	9.0	8.0	90	3.1-2.5	220
Mean Llea	16/4/92	2.40016	1.6E-04	0.07894	1.5E-05	0.06767	1.1E-04	0.0002	0.0001	-18.61	0.08	30.18	0.002	8.0	6.5	65	4.7-2.6	210
Mean Llea	16/4/92	2.40128	3.2E-04	0.06857	3.8E-05	0.06592	2.2E-04	0.0002	0.0002	-18.61	0.08	30.18	0.019	9.5	7.0	70	3.2-1.2	240
Min		2.38857	1.0E-05	0.05737	1.5E-05	0.06513	4.0E-05	0.0001	0.0001	-19.64	0.04	23.46	0.002	8.0	6.0	65		0
Max		2.40128	8.5E-04	0.26433	7.0E-04	0.06767	2.8E-04	0.0017	0.0004	-18.59	0.09	63.82	0.083	10.5	9.5	100		240
Mean		2.39764	3.6E-04	0.11073	1.2E-04	0.06629	1.4E-04	0.0004	0.0002	-18.99	0.07	45.17	0.014	8.9	7.7	84		173
Stdev		0.00475	3.2E-04	0.07045	2.3E-04	0.00096	7.5E-05	0.0005	0.0001	0.47	0.02	15.56	0.028	1.0	1.2	13		90

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(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Broadhaven site 1993.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Broadhaven	21/2/93	2.36129	2.8E-04	0.11968	8.6E-04	0.06276	2.7E-04	0.282	2.1E-13	-19.43	0.042	40.31	7.5	6.5	90	4.2-3.2	320
Broadhaven	21/2/93	2.34581	3.2E-04	0.09165	1.2E-03	0.06683	2.8E-05	0.259	1.2E-15	-19.43	0.042	40.31	7.5	6.5	90	5.7-3.6	320
Broadhaven	22/2/93	2.34581	3.2E-04	0.09165	1.2E-03	0.06683	2.8E-05	0.259	5.3E-13	-18.68	0.018	31.50	7.5	7.5	100	3.7-1.7	340
Broadhaven	23/2/93	2.36821	4.1E-04	0.29045	4.1E-05	0.06453	2.8E-05	0.956	5.3E-14	-18.77	0.041	31.50	6.0	5.0	90	3-0	80
Broadhaven	23/2/93	2.35977	6.4E-04	0.51637	1.5E-03	0.06480	2.8E-04	3.2	1.4E-12	-18.77	0.041	64.74	6.0	5.0	90	3-0	80
Broadhaven	24/2/93	2.36547	1.5E-04	0.11435	9.6E-05	0.06311	1.4E-05	0.312	3.1E-14	-19.79	0.032	64.74	7.0	5.5	80	5-2.5	220
Broadhaven	24/2/93	2.41089	3.7E-04	0.34189	3.1E-05	0.06420	6.8E-05	1.06	6.9E-14	-19.79	0.032	37.55	7.5	5.5	83	3.4-2.3	220
Min		2.34581	1.5E-04	0.09165	3.1E-05	0.06276	1.4E-05	0.26	1.2E-15	-19.79	0.018	31.50	6.0	5.0	80		80
Max		2.41089	6.4E-04	0.51637	1.5E-03	0.06683	2.8E-04	3.20	1.4E-12	-18.68	0.042	64.74	7.5	7.5	100		340
Mean		2.36532	3.6E-04	0.22372	6.9E-04	0.06472	1.0E-04	0.90	3.3E-13	-19.24	0.035	44.38	7.0	5.9	89		226
Stdev		0.02196	1.5E-04	0.16418	6.2E-04	0.00161	1.2E-04	1.07	5.1E-13	0.49	0.009	14.38	0.7	0.9	6		111

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(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Rhoscrowther site 1993.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Rhoscrowther	22/2/93	2.40485	9.5E-04	0.19558	8.4E-05	0.06334	1.7E-04	0.494	3.3E-14	-18.97	0.190	43.69	8.5	8.0	95	7.9-2.7	340
Rhoscrowther	23/2/93	2.41259	4.0E-04	0.08573	7.1E-04	0.06301	3.0E-04	0.193	1.6E-13	-20.26	0.041	63.91	6.0	5.0	90	4.1-1.4	60
Rhoscrowther	24/2/93	2.41771	4.4E-04	0.18440	1.6E-03	0.06300	3.0E-04	0.54	4.2E-13	-20.37	0.079	46.48	7.5	5.5	80	3.1-0.2	220
Min		2.40485	4.0E-04	0.08573	8.4E-05	0.06300	1.7E-04	0.19	3.3E-14	-20.37	0.041	43.69	6.0	5.0	80		60
Max		2.41771	9.5E-04	0.19558	1.6E-03	0.06334	3.0E-04	0.54	4.2E-13	-18.97	0.190	63.91	8.5	8.0	95		340
Mean		2.41172	6.0E-04	0.15524	8.0E-04	0.06312	2.5E-04	0.41	2.1E-13	-19.87	0.103	51.36	7.3	6.2	88		207
Stdev		0.00648	3.1E-04	0.06045	7.6E-04	0.00020	7.5E-05	0.19	2.0E-13	0.78	0.077	10.96	1.3	1.6	8		140

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(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Mean Llea site 1993.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Mean Llea	25/2/93	2.38879	2.6E-04	0.25504	2.2E-03	0.06691	2.9E-04	0.29	5.8E-13	-18.93	0.030	64.74	7.0	7.0	100	9.4-4.2	220
Mean Llea	25/2/93	2.39186	6.3E-04	0.47568	8.3E-05	0.06556	2.7E-04	0.4	9.1E-13	-18.93	0.030	48.14	5.0	5.0	100	10.1-9.4	220
Mean Llea	25/2/93	2.39000	3.6E-04	0.49563	1.2E-02	0.06500	1.7E-04	0.0617	1.4E-12	-18.93	0.030	62.25	2.0	2.0	100	10.1-9.4	220
Mean Llea	26/2/93	2.39955	9.1E-04	0.17440	8.8E-05	0.06566	1.5E-04	0.224	1.6E-11	-19.61	0.020	35.08	1.0	1.0	100	5-1.8	300
Mean Llea	26/2/93	2.40636	5.0E-04	0.13536	5.6E-03	0.06637	1.6E-04	0.0669	5.6E-13	-19.61	0.020	35.08	3.0	2.5	95	3.1-0.5	0
Mean Llea	27/2/93	2.39554	1.4E-04	0.18344	4.1E-05	0.06529	3.9E-05	0.0639	3.1E-14	-18.72	0.064	68.89	4.0	3.5	95	7-4.5	350
Mean Llea	27/2/93	2.39910	5.0E-04	0.17735	2.2E-04	0.06515	1.5E-04	0.077	3.3E-14	-18.72	0.064	68.89	3.0	2.0	90	7.1-3.6	340
Mean Llea	27/2/93	2.39841	5.3E-04	0.21470	4.2E-04	0.06576	1.5E-04	0.077	1.3E-13	-18.72	0.064	68.89	1.0	-0.5	85	7.2-5.6	300
Min		2.38879	1.4E-04	0.13536	4.1E-05	0.06500	3.9E-05	0.06	3.1E-14	-19.61	0.020	35.08	1.0	-0.5	85		0
Max		2.40636	9.1E-04	0.49563	1.2E-02	0.06691	2.9E-04	0.40	1.6E-11	-18.72	0.064	68.89	7.0	7.0	100		350
Mean		2.39620	4.8E-04	0.26395	2.6E-03	0.06571	1.7E-04	0.16	2.4E-12	-19.02	0.040	56.50	3.3	2.8	96		244
Stdev		0.00586	2.4E-04	0.14119	4.4E-03	0.00064	7.9E-05	0.13	5.5E-12	0.38	0.020	14.88	2.1	2.3	6		112

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(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Swansea site 1993.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Swansea	1/3/93	2.39743	1.1E-03	0.39744	3.4E-03	0.06239	2.2E-04	15	1.8E-12	-19.82	0.024	36.56	5.0	4.0	90	3-0.1	300
Swansea	1/3/93	2.39246	4.5E-04	0.29941	5.7E-05	0.06439	4.5E-04	10	1.7E-13	-19.82	0.024	36.56	5.0	4.0	90	3-0.1	290
Swansea	2/3/93	2.41020	1.9E-04	0.12545	1.6E-05	0.06403	5.6E-05	13.8	1.8E-13	-19.49	0.028	36.56	5.5	3.5	80	0.7-0	40
Swansea	2/3/93	2.40172	1.3E-03	0.14344	5.6E-05	0.06367	2.8E-04	14.1	2.7E-14	-19.49	0.028	36.56	5.5	3.5	80	0.7-0	40
Swansea	3/3/93	2.40013	1.5E-04	0.13585	4.7E-05	0.06412	2.9E-04	13.7	1.9E-13	-18.18	0.044	29.18	5.0	3.0	80	2-1.6	120
Swansea	3/3/93	2.39991	7.1E-04	0.14378	3.1E-05	0.06391	3.2E-04	8.75	1.0E-13	-18.18	0.044	29.18	5.0	3.0	80	2-1.6	120
Swansea	4/3/93	2.38655	6.4E-04	0.35228	5.2E-04	0.06417	7.1E-05	13.5	2.7E-13	-19.62	0.056	31.86	6.0	3.0	70	3-0	300
Swansea	4/3/93	2.39704	7.7E-04	0.17756	4.0E-05	0.06419	1.1E-04	4.99	2.9E-14	-19.62	0.056	31.86	6.0	3.0	70	3-0	300
Min		2.38655	1.5E-04	0.12545	1.6E-05	0.06239	5.6E-05	4.99	2.7E-14	-19.82	0.024	29.18	5.0	3.0	70		40
Max		2.41020	1.1E-03	0.39744	3.4E-03	0.06439	4.5E-04	15.00	1.8E-12	-18.18	0.056	36.56	6.0	4.0	90		300
Mean		2.39818	6.4E-04	0.22190	5.3E-04	0.06386	2.2E-04	11.75	3.5E-13	-19.28	0.038	33.54	5.4	3.4	80		189
Stdev		0.00690	3.6E-04	0.11003	1.2E-03	0.00063	1.4E-04	3.48	6.1E-13	0.69	0.014	3.38	0.4	0.4	8		120

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(continued)

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for each south Wales sample site 1992 and 1993.

Tabulated carbon and lead concentration and isotopic composition values with weather parameters for the Port Talbot site 1993.

Location	Date	$^{208}Pb/^{207}Pb$	Erorr	$^{207}Pb/^{206}Pb$	Erorr	$^{204}Pb/^{207}Pb$	Erorr	Pb concentration (ng/m3)	Error	$\delta^{13}C$	Erorr	Carbon concentration (µg/cm3)	Dry Temp (°C)	Wet Temp (°C)	Relative humidity (%)	Wind speed (m/sec)	Wind dir (°)
Port Talbot	1/3/93	2.43449	1.4E-03	0.46873	1.6E-02	0.07023	4.0E-04	2.3	1.2E-11	-21.67	0.039	38.29	4.0	2.0	80	5.8-2.9	300
Port Talbot	1/3/93	2.42468	2.8E-04	0.53623	7.5E-05	0.06451	4.6E-05	3.7	1.9E-13	-21.67	0.039	38.29	4.0	2.0	80	5.8-2.9	300
Port Talbot	2/3/93	2.42013	6.6E-04	0.26079	7.5E-05	0.06471	1.5E-04	0.822	5.3E-14	-19.52	0.051	24.46	5.5	3.5	80	1-0	40
Port Talbot	2/3/93	2.42006	1.2E-03	0.18437	7.6E-04	0.05726	2.4E-04	0.478	2.1E-13	-18.30	0.021	24.46	5.5	3.5	80	1-0	40
Port Talbot	3/3/93	2.42013	4.0E-03	0.32090	1.3E-03	0.06445	3.2E-04	1.2	4.0E-13	-22.16	0.019	26.46	5.0	2.0	80	1.6-0.2	120
Port Talbot	3/3/93	2.43196	5.7E-03	0.47912	5.6E-04	0.06959	5.2E-04	16	1.1E-13	-22.16	0.019	26.46	5.0	2.0	80	1.6-0.2	120
Port Talbot	4/3/93	2.42918	1.4E-04	0.56781	1.9E-04	0.06438	6.7E-04	1.56	1.3E-12	-27.37	0.020	22.53	6.5	3.0	75	3.3-0	300
Port Talbot	4/3/93	2.42689	2.2E-03	0.27831	5.7E-04	0.06492	5.1E-05	3.62	1.4E-13	-27.37	0.020	22.53	6.5	3.0	75	3.3-0	300
Port Talbot	5/3/93	2.42097	6.3E-04	0.19621	6.7E-04	0.05769	8.2E-05	5	4.7E-14	-21.26	0.064	24.46	6.0	5.0	90	5.8-0.3	320
Port Talbot	5/3/93	2.43617	7.9E-04	0.45634	2.3E-04	0.06998	7.2E-05	9	7.6E-14	-21.26	0.064	24.46	6.0	5.0	90	5.8-0.3	320
Min		2.42006	1.4E-04	0.18437	7.5E-05	0.05726	4.6E-05	0.48	4.7E-14	-27.37	0.019	22.53	4.0	2.0	75		40
Max		2.43617	5.7E-03	0.56781	1.6E-02	0.07023	6.7E-04	16.00	1.2E-11	-18.30	0.064	38.29	6.5	5.0	90		320
Mean		2.42646	1.7E-03	0.37488	2.0E-03	0.06477	2.6E-04	4.37	1.5E-12	-22.27	0.036	27.24	5.4	3.1	81		216
Stdev		0.00625	1.8E-03	0.14261	4.8E-03	0.00456	2.2E-04	4.81	3.9E-12	2.95	0.019	5.97	0.9	1.2	5		120